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Melpar, Inc., Falls Church, Va.

T TESTING OF ABLATION MATERIAL

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→ PRELIMINARY DATA CONCERNING

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FOREWORD

This report presents NASA with preliminary data for the thermo-physical properties of ablative materials 1, 2, 3, and 4 in the nondegraded state. The data specific heat is complete. In the case of the remaining properties, thermal conductivity, thermal expansion, tensile strength, and compressive strength there remains some data points to be taken. The information submitted does however, define the characteristics over most of the usable temperature range. Also submitted is a separate test method report defining the test techniques utilized to obtain this data.

1. INTRODUCTION

The overall objective of this test program is to define the basic characteristics of ablative materials in two conditions and temperature ranges. The nondegraded materials are to be evaluated for both thermal and mechanical properties throughout the temperature range from -200°F to $+750^{\circ}\text{F}$. Once these properties have been defined, to assist in basic application design, the overall performance of the ablated materials after exposure to a plasma jet is to be evaluated throughout the temperature range from 1000°F to 5000°F .

The technical staff of NASA established the usable temperature range of interest for the nondegraded material on the basis of thermal gravimetric analysis, or weight loss determination. This represents a realistic criteria in terms of the anticipated environment which will impose an extremely rapidly increasing surface temperature on the material. Unfortunately, the available test methods normally used to measure the properties of interest are based upon the establishment of equilibrium temperatures throughout a given specimen. As a consequence, it becomes necessary to use a slower heating rate than the 100°F per minute rate used by NASA to determine weight loss characteristics.

The ablative materials to be tested under this contract have been specifically formulated to take advantage of the available heat of vaporization as a means of thermal protection under a re-entry condition.

Of necessity, then, the protective materials are composed of highly reactive organic polymers that are extremely unstable in a high

thermal environment. This situation in itself would not present undue difficulties, but the fact that the thermal diffusivity of these materials is extremely low means that at temperatures above 400°F, it is not possible to drive the available heat into a specimen fast enough to realize a uniform temperature without first experiencing chemical reactions on the surface. This reaction is a combination of vaporization and chemical decomposition; such that the surface becomes molten, while the center of the specimen remains relatively cool.

The performance of the required property measurements dictates a heating rate that is not truly representative of the actual environment to be experienced in application. Further, the interpretation of the resulting data makes it necessary to redefine the "usable" temperature range in terms of each specific property.

In performing the required property measurements, Melpar has modified the experimental method slightly, and attempted to relate the resulting data as nearly as possible to its true significance in view of the desired application. The total discussion concerning this material evaluation program is not presented in this report. The intent of this report is only to provide the agency with the basic data obtained to date, and reserve a detailed discussion and conclusion for the final report after all of the data has been gathered and it is possible to relate all of the properties to the total material behavior as a function of temperature.

In the following sections the data is presented for each property.

2.0 SPECIFIC HEAT

Specific heat determinations have been completed on all four materials; high density phenolic, low density phenolic, silicone resin, and silicone resin impregnated honeycomb. In reporting this data, both tabular and graphical data is presented. This includes both enthalpy and specific heat information. In the case of the phenolic material, a graph is presented showing both high and low density together, which verifies that both were formulated from the same material. Similarly, the composite data for the silicone resin and the silicone resin impregnated honeycomb is shown together, indicating that the main contribution in the mechanism of specific heat results from the silicone resin in the composite.

In all cases, it was necessary to stabilize the sample at the test temperature for a period of one half hour to insure equilibrium. In conducting these tests, it was necessary to weigh the sample both before and after each drop. For further information, then, a set of graphs are also presented to show the weight loss as a function of temperature for one half hour exposure periods in an open system.

During the first experiments of this effort, Melpar made a series of temperature drops in a closed system. The sample was sealed in a welded capsule. This provided a rather interesting effect, for the same sample was dropped at each temperature, and each successive exposure allowed slightly more material to vaporize. The trapped gases, then,

established a pressure equilibrium that resulted in some undefined transitions, as the thermochemical reactions took place. This data is also presented.

The calibration data obtained for the ice calorimeter is presented only in tabular form. This was accomplished using NBS standard Al_2O_3 . The calibration method is described in detail in the test method report.

The mean experimental accuracy of the enthalpy determination is ± 0.85 percent. The inhomogeneity of the sample material, however, results in a mean experimental accuracy of only ± 3 percent in the calculation of specific heat. This is due to the fact that each specimen seemed to react to a different degree as a consequence of temperature exposure.

All of the specific heat data is presented in appendix A.

3.0 THERMAL EXPANSION

In performing the measurement of thermal expansion of materials 1, 2, 3, and 4 Melpar found it impossible to obtain a continuous curve for the expansion characteristics from -200°F to $+750^{\circ}\text{F}$. This was due to the same problem that confronted the specific heat measurement; extremely low diffusivity. It was not possible to drive the furnace temperature at a controlled rate, to experience a heating rate of the specimen anywhere near the desired 100°F per minute requested by NASA.

In order to achieve as rapid a heating rate as possible it was necessary to stabilize the test chamber at the test temperature and load the dilatometer directly into the chamber.

As indicated in the introduction of this report, the interpretation of this data dictates a definition of the maximum usable temperature of the materials under test relative to the thermal environment.

At temperatures somewhat below 400°F , it is possible to obtain valid thermal expansion data for all of the materials. This is based upon the fact that the sample reaches equilibrium at the temperature rapidly enough that little if any degradation or reaction has occurred.

The determination of thermal expansion at temperatures above this level becomes an extremely complex situation. If the test chamber is stabilized at the desired test temperature above 400°F , the sample cannot possibly obtain equilibrium at the furnace temperature without severe reaction and degradation of the entire sample surface. The sample surface rapidly achieves the reaction temperature of the material,

with the majority of the available thermal energy transformed into heat of vaporization and reaction such that the inside surface of the reaction boundary layer moves slowly to the center of the sample.

By the time the total sample reaches the test temperature, the reaction products have formed a viscous composition that flows out of the specimen. This reaction product is of a much lower density than the starting material, and is quickly confined by the restraining walls of the outer quartz tube, and contributes an extremely large volume expansion component which completely overrides any available contribution by the base material component of linear thermal expansion; consequently, the sample expansion curve realizes an extremely abrupt inflection point. If a full set of data points are taken at the remaining elevated test temperature by this method, the curve realizes a peak value at some temperature slightly above 400°F, and then drops off rapidly above this peak temperature, for at the higher temperatures, two additional factors contribute to the gross lowering of the amount of thermal expansion. Not only is a far greater portion of the specimen lost through vaporization but the material also becomes extremely plastic and flows readily under the slight pressure of the quartz transmission rod.

The only alternative to obtain representative linear thermal expansion data at temperatures above 400°F is to set the temperature of the test chamber at some level far exceeding the test temperature desired, and to attempt to obtain a quasi-steady state measurement as the specimen approaches the desired test temperature while its surrounding environment

remains at a much higher temperature level. This improves the overall heat transfer to the center of the specimen for the rate of conduction is dependent upon the thermal diffusivity, which is in turn a function of the thermal gradient.

Unfortunately, the use of a quartz dilatometer is confined to a maximum temperature of 1000°C. This is not adequate to force the specimen to heat up so rapidly as to eliminate thermal reaction of the surface. Further, this situation presents a wide range of variables which still do not represent the intended application.

For these reasons, Melpar feels that only the thermal expansion data in the range of -200°F to +400°F is representative of the material characteristics. At temperatures above this level, an attempt has been made to relate the true linear thermal expansion characteristics to the elevated temperature environment, but this data can only present a trend, and an insight into the overall mechanisms present in this situation. Any effort to consider this information to be an accurate measure of linear thermal expansion would be completely in error.

The data concerning the expansion characteristics and behavior throughout the full temperature range from -200°F to +400°F is presented in both tabular and graphical form in the following pages. The remaining higher temperature data will be presented in the final report. Again, it must be emphasized that data above 400°F will be presented only to provide an insight into the interpretation of the basic mechanisms, and not as an absolute measure of this property, for at these temperatures the

linear thermal expansion is only a minor effect compared to the thermo-chemical reaction involved.

The thermal conductivity data is presented in appendix B.

4.0 THERMAL CONDUCTIVITY

In the previous sections of this report, the overall problems associated with the measurement of the material properties have been discussed in some detail. In all cases, the major difficulty lies in the fact that once a sample has been introduced in a temperature environment in excess of 400°F, a time dependent chemical reaction begins.

This continues to be a problem in the measurement of thermal conductivity, for this determination is dependent upon the establishment of a uniform steady state equilibrium condition. As a consequence of the chemical reaction at the surface of the specimen, and the fact that the vaporization process becomes a temperature limiting mechanism, it is almost impossible to force a desired thermal gradient within the specimen prior to complete sample degradation. This results in thermal conductivity data that is a measure of only the degraded residue, rather than the virgin material.

The data obtained to date is reported in appendix C.

5.0 MECHANICAL PROPERTY DATA

The materials as received from the agency were found to exhibit a high degree of internal stress. This resulted in a very random

failure mode of individual samples, such that it was not possible to confine the failure to the guage length with a normal tensile specimen. Additional effort was expended in modifying the sample design to eliminate this difficulty. When it became apparent that the internal stress would continue to be a problem regardless of sample configuration, Melpar contacted the NASA technical staff and discussed this with them. This meeting established the fact that the size of the molded disks was representative of the thickness and size that would be used in application, so that if internal stresses were in the sample blocks, these same internal stresses would exist in the final designed and fabricated part. Based upon this, it was agreed that these tests would continue with the material as received.

Difficulties have been encountered in application of strain guages, as originally planned, due to surface degradation. Sample failure at other than guage length has also continued; resulting in a large number of invalid test points.

Appendix D presents the data obtained to date for the tensile and compressive properties of the materials.

APPENDIX A

PRELIMINARY
ENTHALPY AND SPECIFIC HEAT
DATA

Table 1

Observed Enthalpy Data for "A" Nylon-Phenolic

<u>Unpressurized</u>		<u>Enthalpy Cal g⁻¹</u>
<u>Temp °F</u>	<u>Specimen</u>	<u>Enthalpy</u>
-191.2	A	30.26
-130.0	"	24.42
-117.5	"	23.34
-112.0	"	22.09
- 22.9	"	9.19
- 4.9	"	6.31
32.0	"	0.00
88.4	"	10.57
293.6	"	57.14
295.4	"	56.24
502.4	"	117.73
509.0	"	118.89
699.8	"	193.33
752.0	"	214.67

Table 2

<u>Pressurized</u>		
293.6	A	58.40
405.1	A	105.28
412.4	A	106.66
558.5	A	166.50
757.4	A	247.10

Table 3

Specific Heat of "A" Nylon-PhenolicsUnpressurizedSpecific Heat B.T.U. per lb per °FSmoothed Values

<u>Temp °F</u>	<u>Specimen</u>	<u>Specific Heat</u>
-200	A	0.165
-150	"	.200
-100	"	.235
- 50	"	.267
0	"	.300
50	"	.331
100	"	.361
150	"	.393
200	"	.423
250	"	.453
300	"	.484
350	"	.513
400	"	.542
450	"	.571
500	"	.599
550	"	.628
600	"	.659
650	"	.684
700	"	.711
750	"	.740

Table 4

Pressurized

297	A	0.730
350	"	"
400	"	"
450	"	"
500	"	"
550	"	"
600	"	"
650	"	"
700	"	"
750	"	"

Table 5

Observed Enthalpy Data for "B" Nylon-Phenolic

<u>Unpressurized</u>		<u>Enthalpy Cal g⁻¹</u>
<u>Temp °F</u>	<u>Specimen</u>	<u>Enthalpy</u>
-184.0	B	30.00
-156.1	"	27.20
-131.8	"	24.22
- 73.0	"	17.10
- 13.0	"	7.55
32.0	"	0.00
75.8	"	8.03
76.1	"	8.16
212.0	"	36.52
293.0	"	55.71
299.0	"	57.63
509.0	"	120.18
689.0	"	188.09
753.8	"	212.96

Table 6

Pressurized

346.1	B	72.22
381.9	"	85.17
391.1	"	88.06
404.6	"	91.71
422.6	"	97.74
439.7	"	103.27
500.9	"	124.30
566.7	"	153.69
753.0	"	248.96

TABLE 7

Specific Heat of "B" Nylon-Phenolic

<u>Unpressurized</u> <u>Smoothed Values</u>		<u>Specific Heat BTU per lb per ° F.</u>	
<u>Temp. ° F</u>	<u>Specimen</u>	<u>Specific Heat</u>	
-200	B	0.165	
-150	"	.200	
-100	"	.235	
- 50	"	.267	
0	"	.300	
50	"	.331	
100	"	.361	
150	"	.393	
200	"	.423	
250	"	.453	
300	"	.484	
350	"	.513	
400	"	.542	
450	"	.571	
500	"	.599	
550	"	.628	
600	"	.659	
650	"	.684	
700	"	.711	
750	"	.740	

TABLE 8

<u>Pressurized</u>		
297	B	0.610
350	"	.610
400	"	.610
450	"	.610
500	"	.610
529	"	.610
530	"	.930
550	"	.930
600	"	.930
650	"	.930
700	"	.930
750	"	.930

TABLE 9

Observed Enthalpy Data for Filled Silicone Resin A

<u>Temp.</u> °F	<u>Specimen</u>	<u>Enthalpy</u>	<u>cal g⁻¹</u>
		<u>Enthalpy</u>	
-202.8	C	43.20	
-202.0	C	43.00	
-195.1	C	41.58	
- 78.7	C	21.05	
- 13.0	C	8.51	
32.0	C	0.00	
113.9	C	15.56	
116.8	C	16.86	
221.0	C	38.13	
320.0	C	57.51	
513.4	C	103.14	
747.5	C	160.37	
753.8	C	161.58	

TABLE 10

Specific Heat of Silicone Resins A

Smoothed Values

Specific Heat BTU per lb per °F.

<u>Temp. °F</u>	<u>Specimen</u>	<u>Specific Heat</u>
-200	C	0.284
-150	"	.301
-100	"	.316
- 50	"	.330
0	"	.340
50	"	.354
100	"	.365
150	"	.372
200	"	.382
250	"	.390
300	"	.396
350	"	.404
400	"	.410
450	"	.415
500	"	.419
550	"	.423
600	"	.427
650	"	.430
700	"	.433
750	"	.435

TABLE 11

Observed Enthalpy Data for Silicone Resin A Honeycomb

Enthalpy Cal ⁻¹ g

<u>Temp. ° F</u>	<u>Specimen</u>	<u>Enthalpy</u>
-202.0	D	42.52
-132.7	D	31.01
- 34.6	D	13.01
- 35.5	D	13.03
- 13.9	D	8.84
32.0	D	0.00
118.4	D	16.73
119.0	D	16.89
224.6	D	38.82
321.9	D	58.81
322.4	D	58.82
520.4	D	104.52
752.0	D	161.09
762.8	D	164.16

Table 12

Specific Heat of Silicone Resin A HoneycombSmoothed ValuesSpecific Heat B.T.U. per lb. per °F

<u>Temp° F</u>	<u>Specimen</u>	<u>Specific Heat</u>
-200	D	0.284
-150	"	.301
-100	"	.316
- 50	"	.330
0	"	.340
50	"	.354
100	"	.365
150	"	.372
200	"	.382
250	"	.390
300	"	.396
350	"	.404
400	"	.410
450	"	.415
500	"	.419
550	"	.423
600	"	.427
650	"	.430
700	"	.433
750	"	.435

Table 13

Calibration of Bunsen Ice Calorimeter Using
National Bureau of Standards Al_2O_3 .

Temp °F	Observed	Calculated	Diff. Percent	Calibration Cal g^{-1}
-193.0	23.93	23.96	-0.13	Nylon-Phenolic Test
411.0	44.79	44.99	- .40	
752.0	94.40	94.68	.30	
-146.0	19.33	19.41	0.41	Silicone Resin Test
752.0	94.38	94.68	.32	

Reference to Test Method

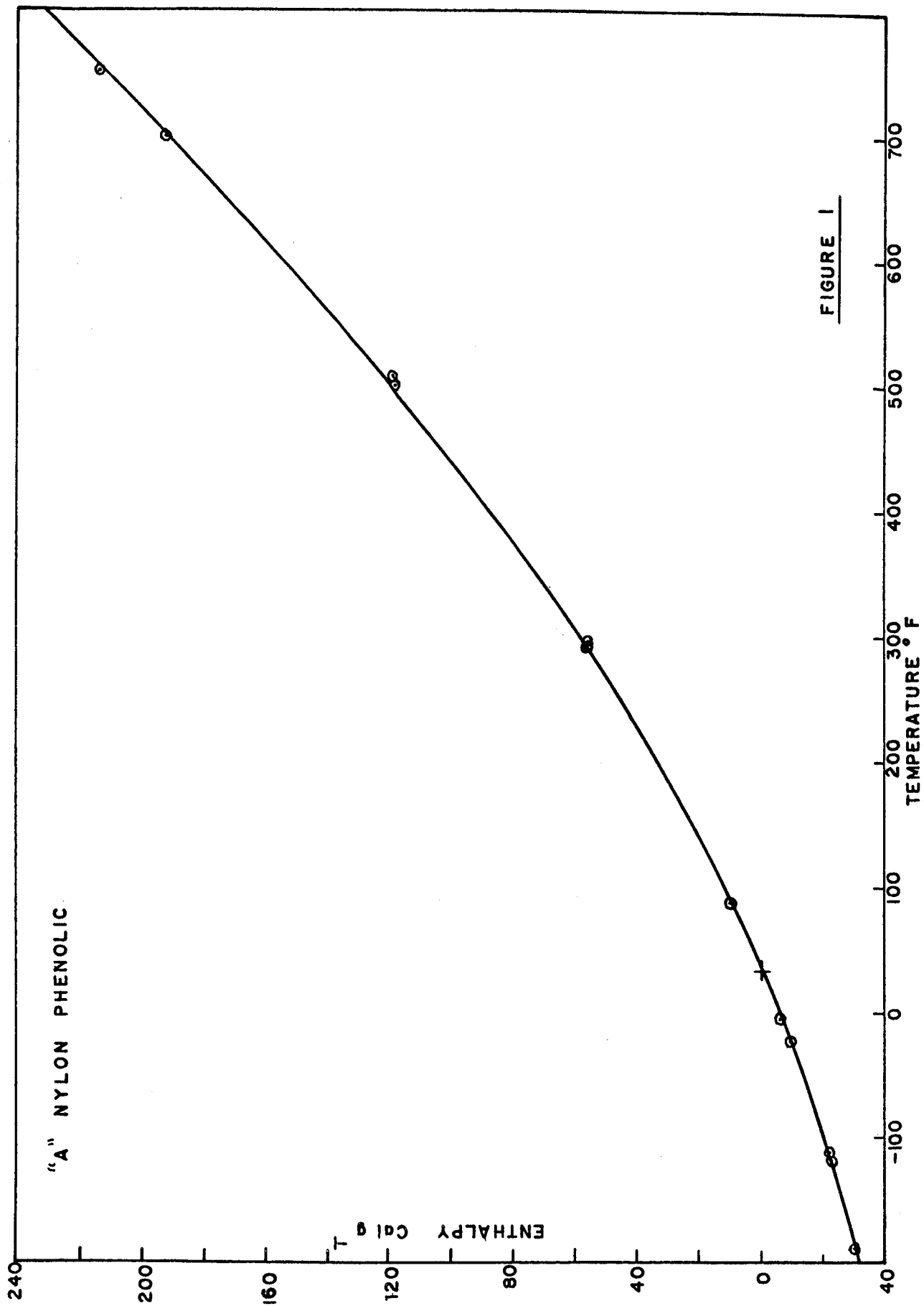
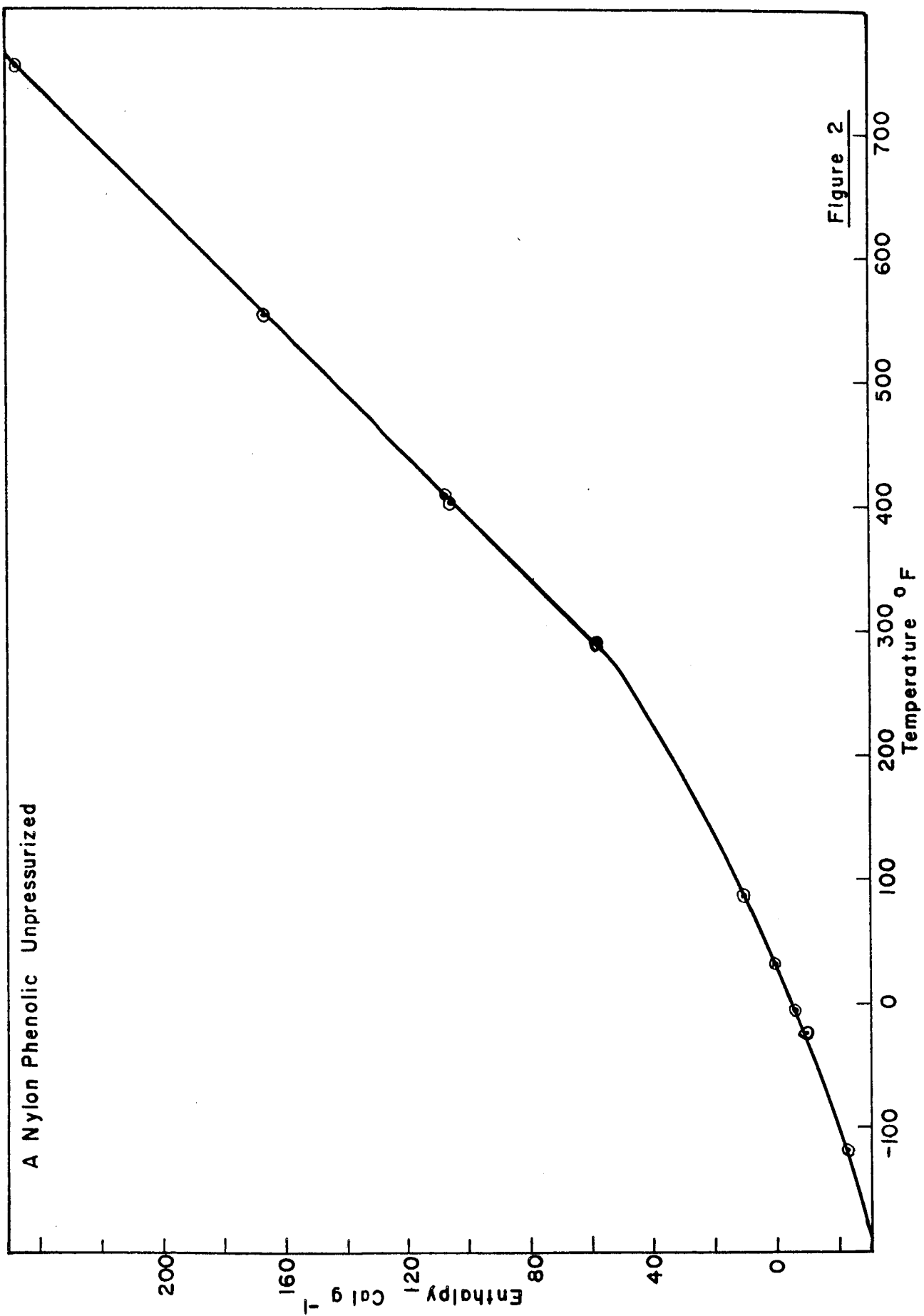


FIGURE 1



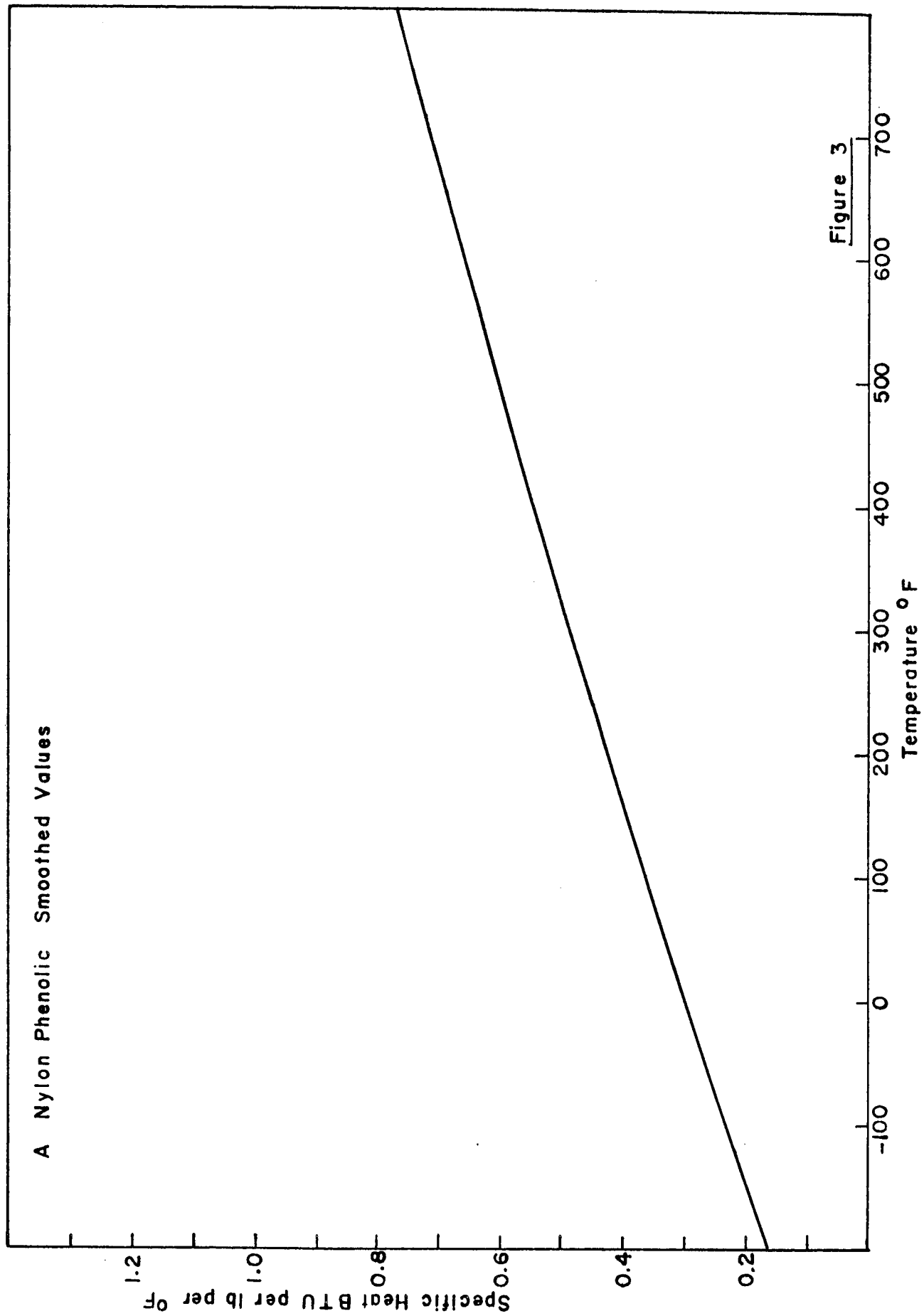
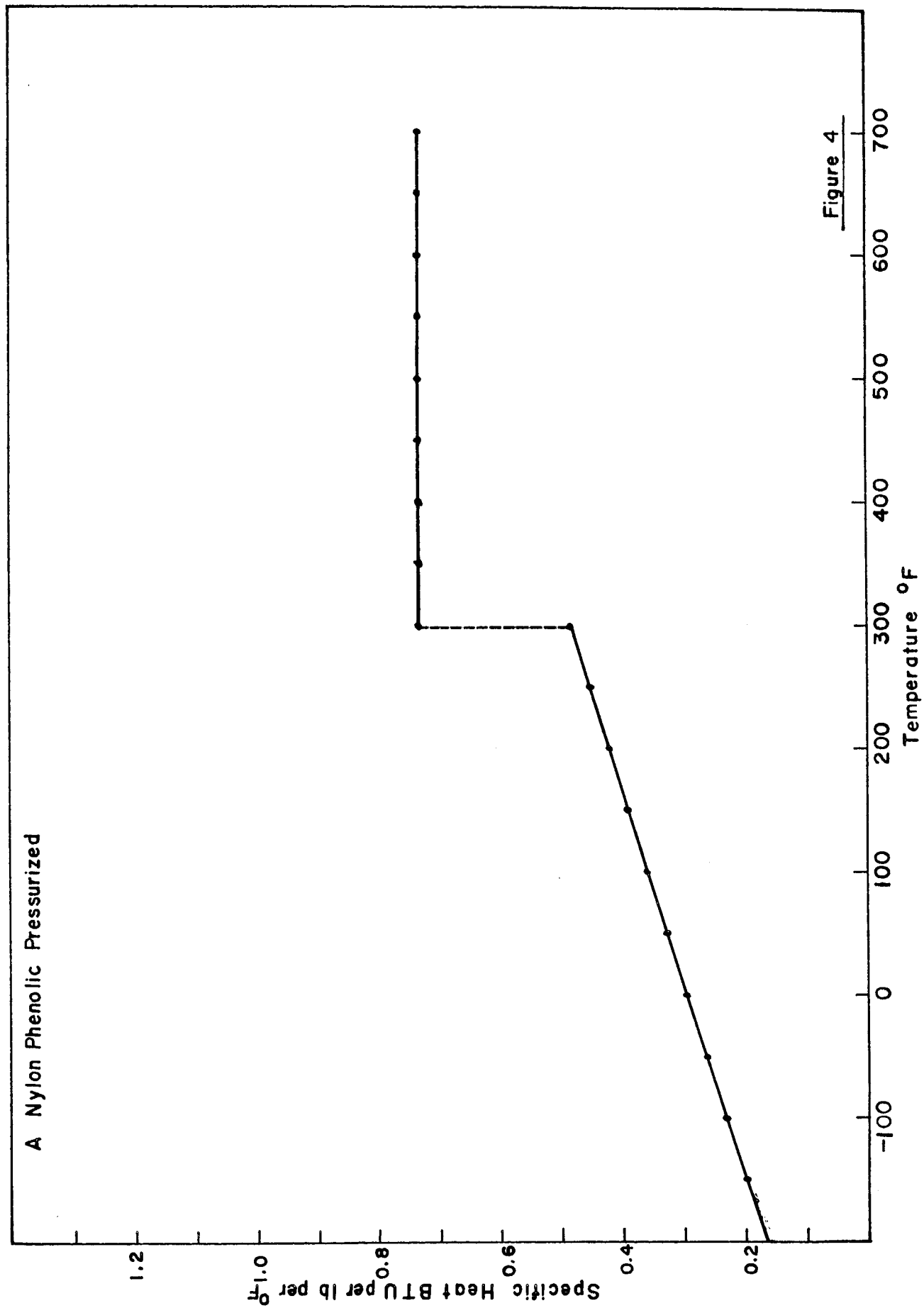


Figure 3



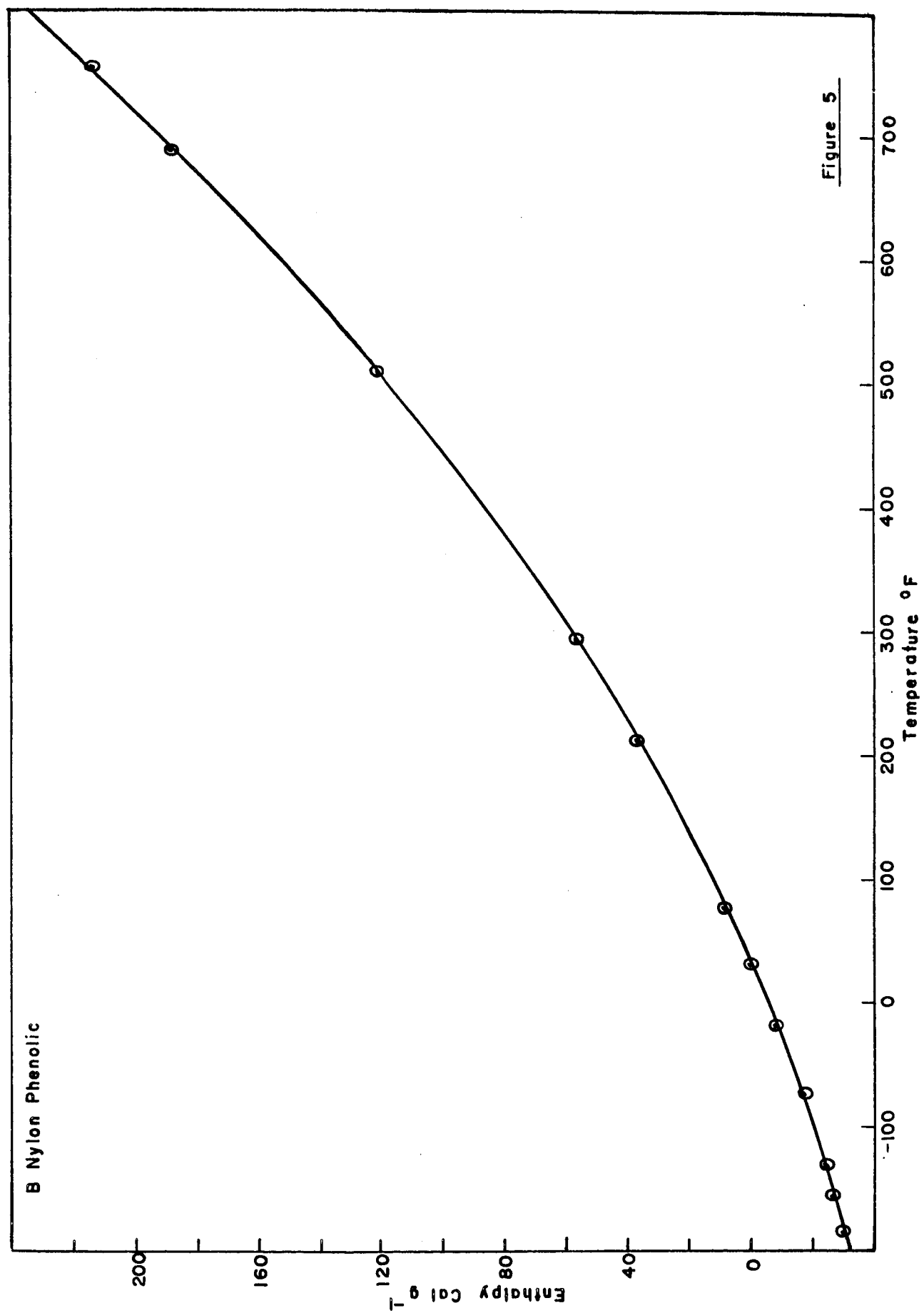
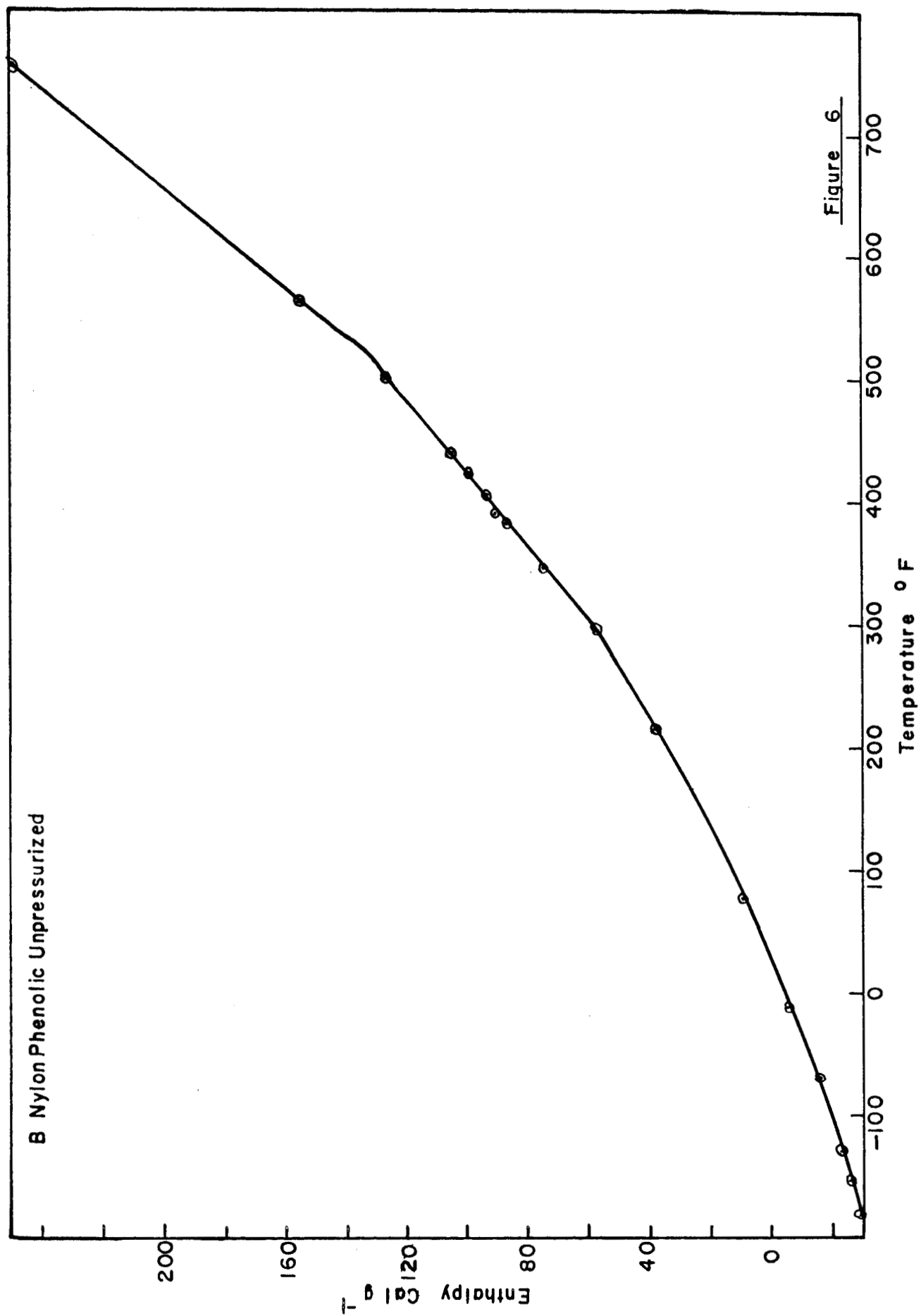


Figure 5



B Nylon Phenolic Smoothed Values

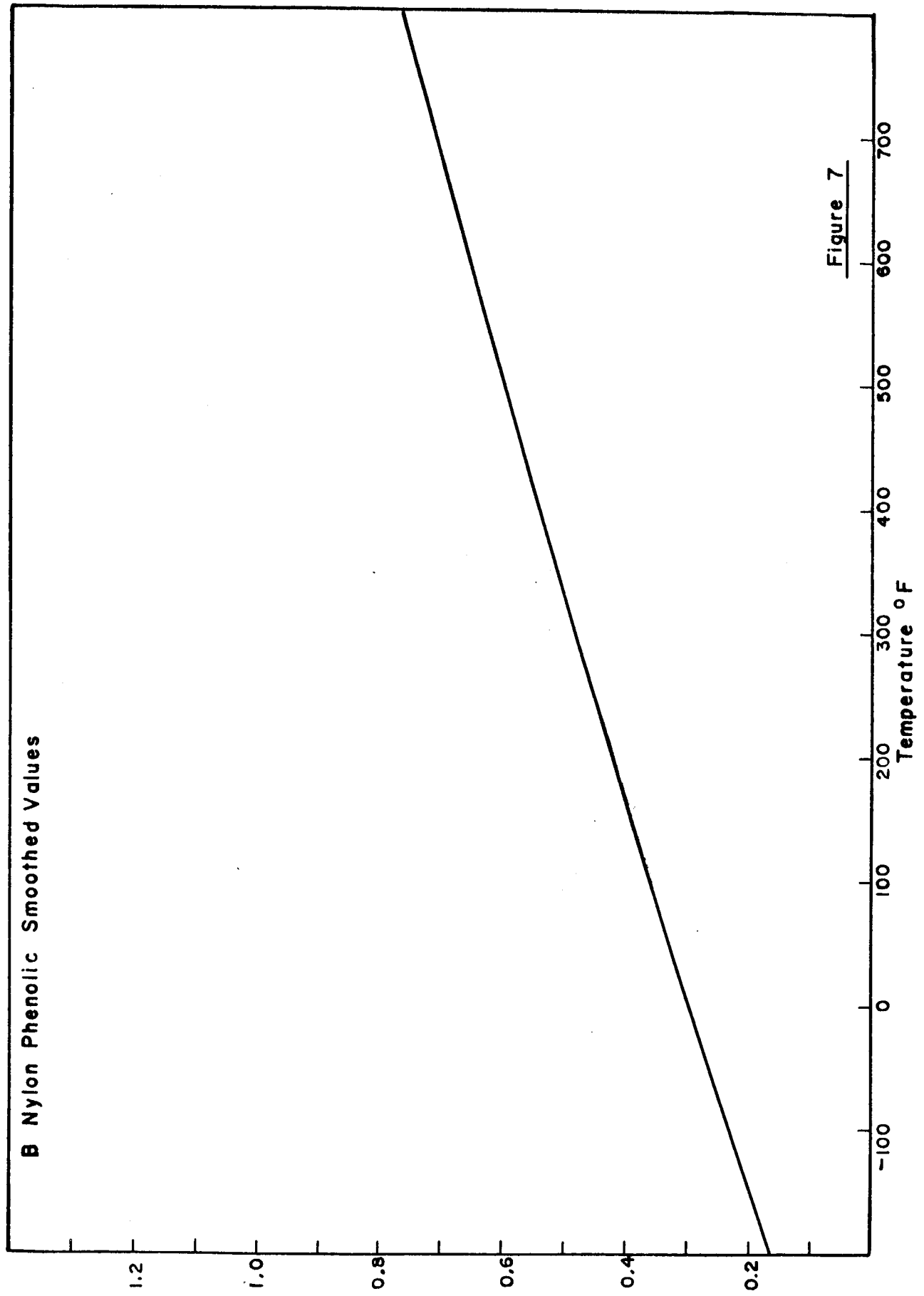


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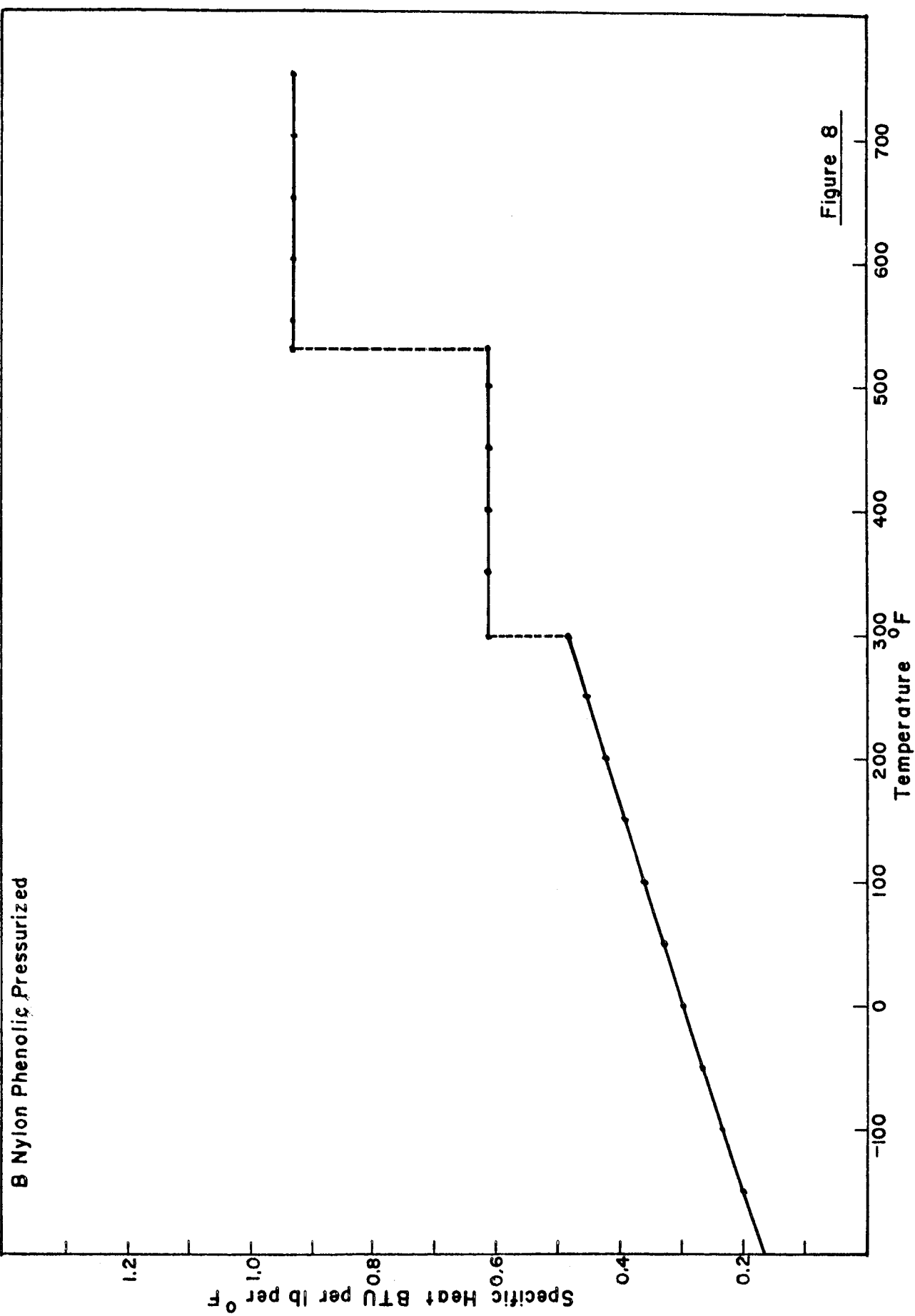


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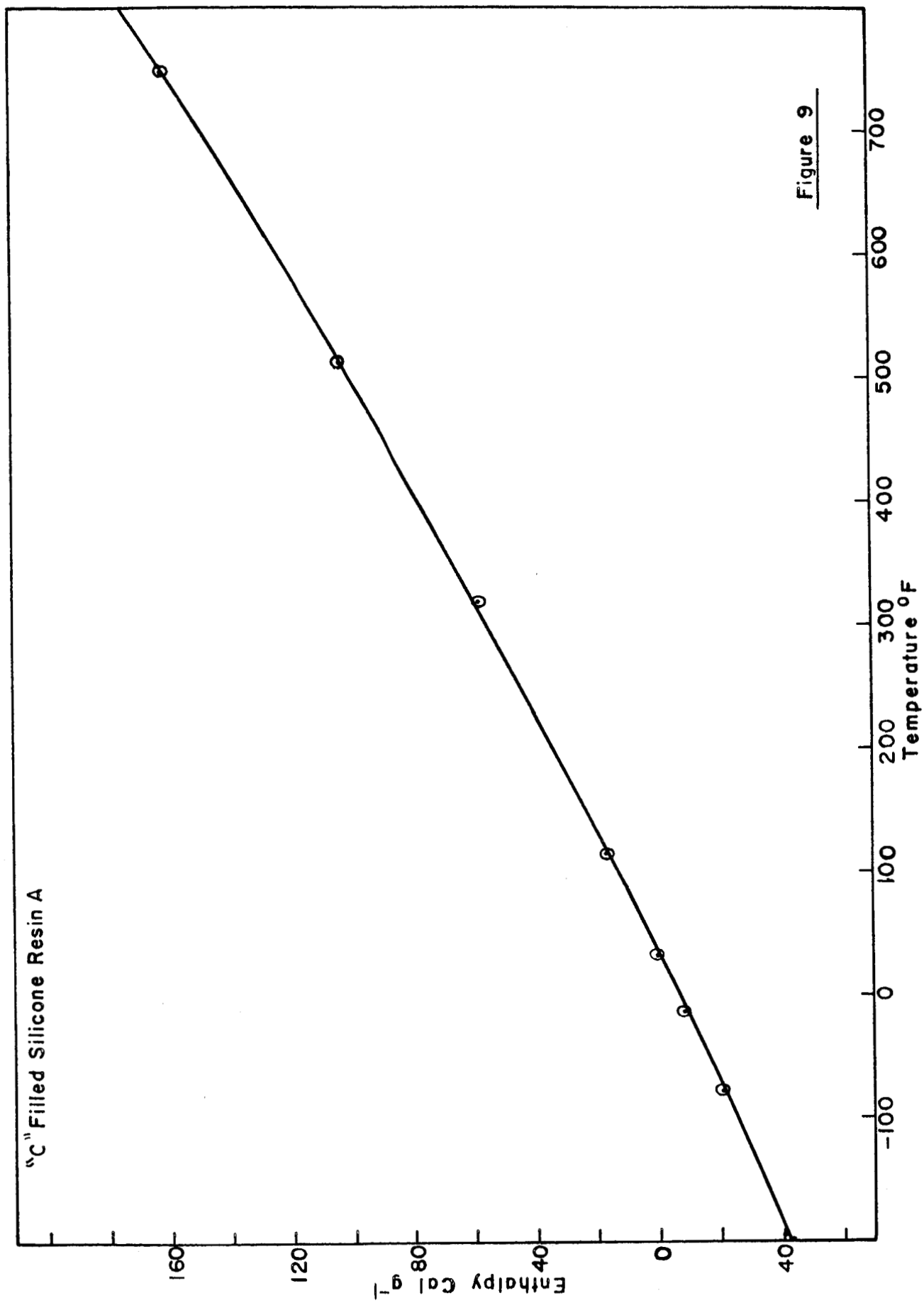


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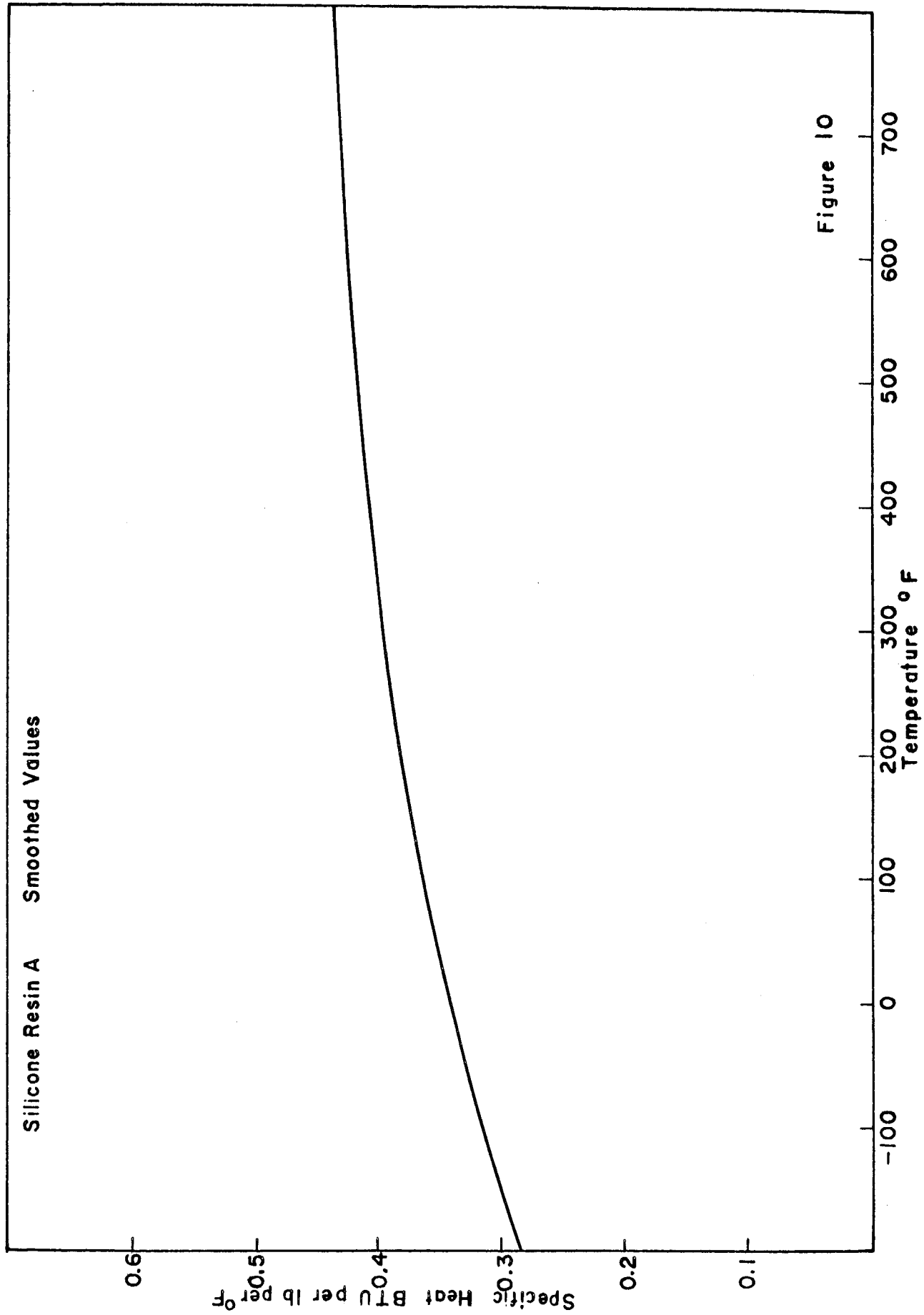


Figure 10

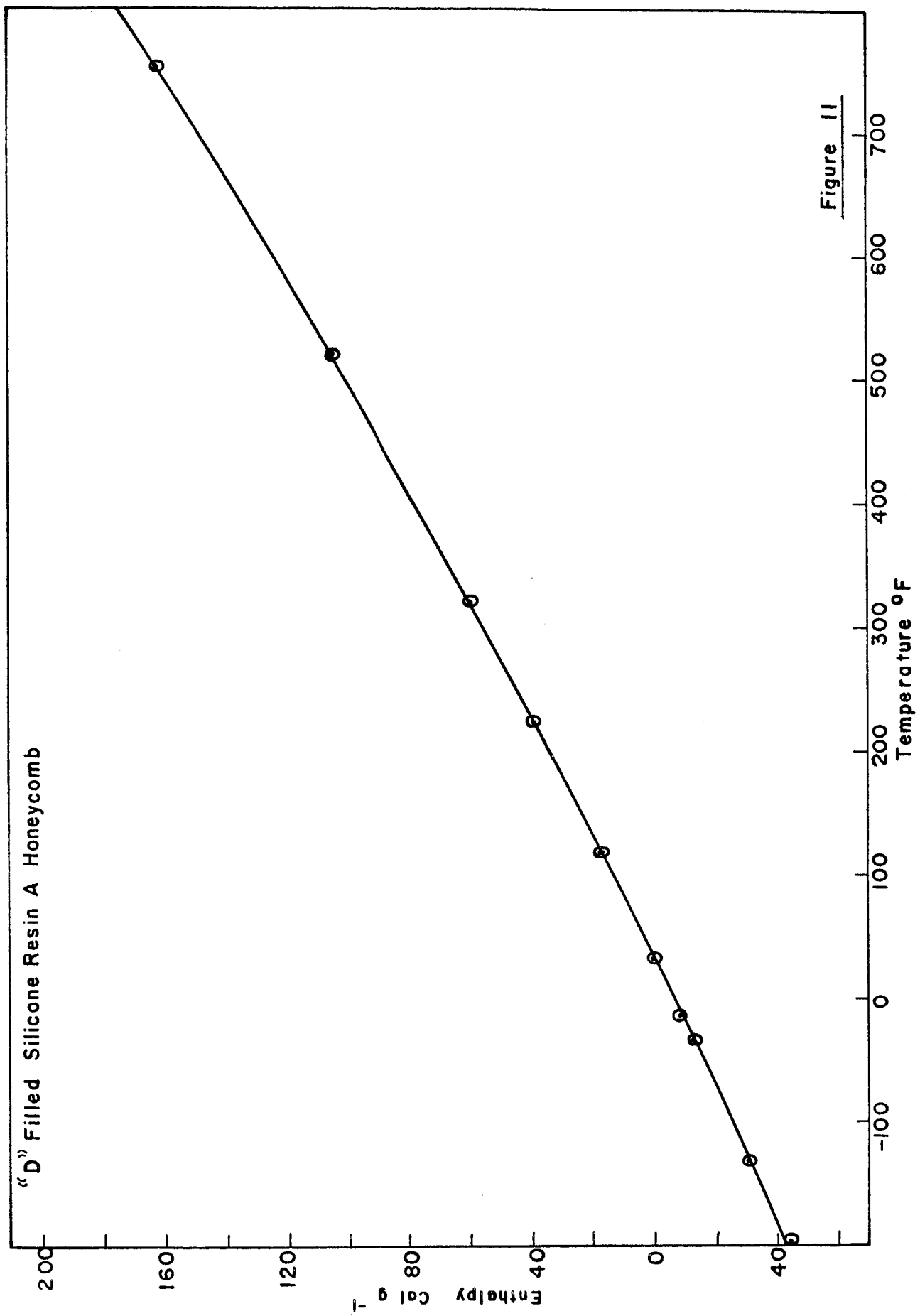


Figure 11

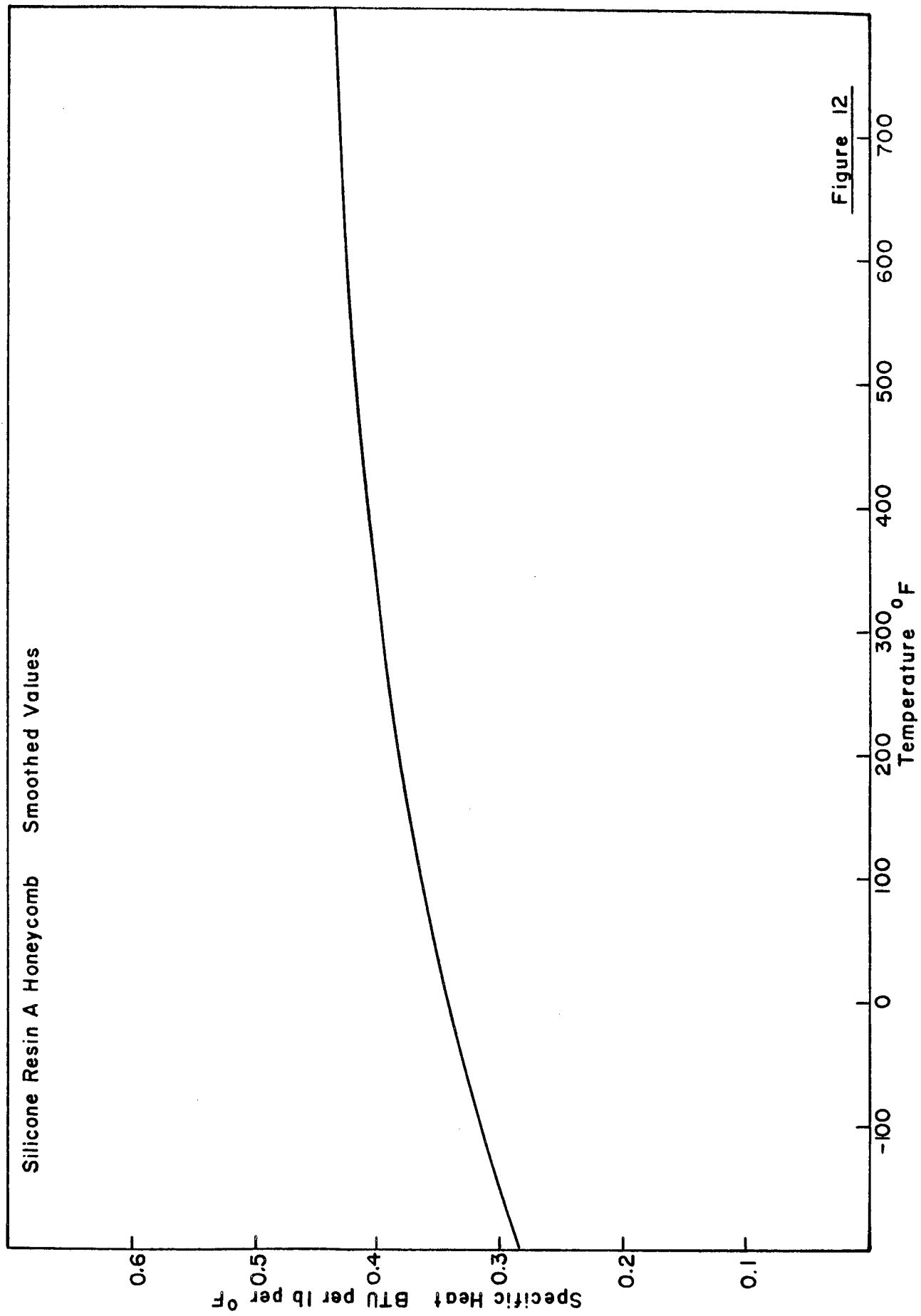


Figure 12

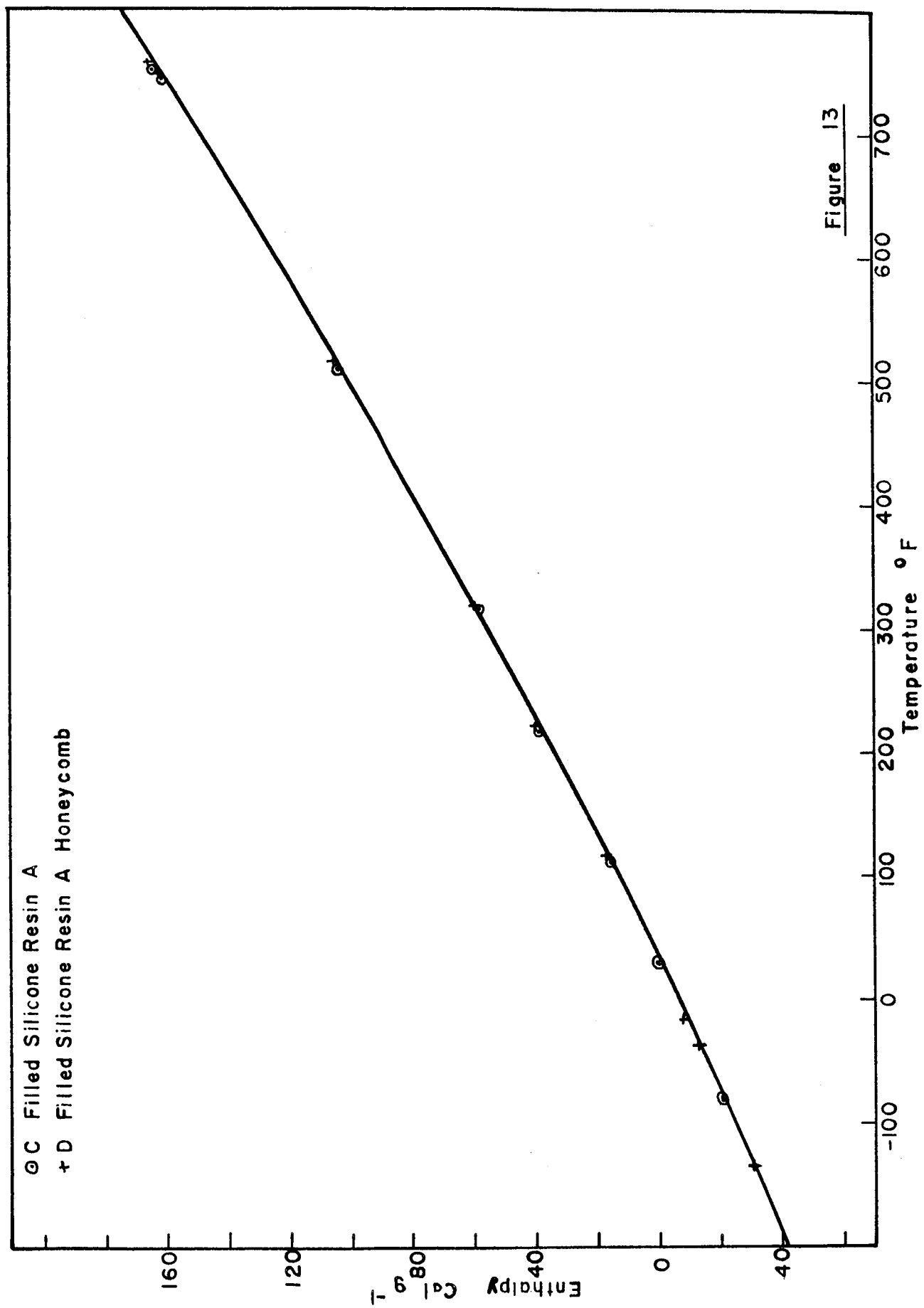


Figure 13

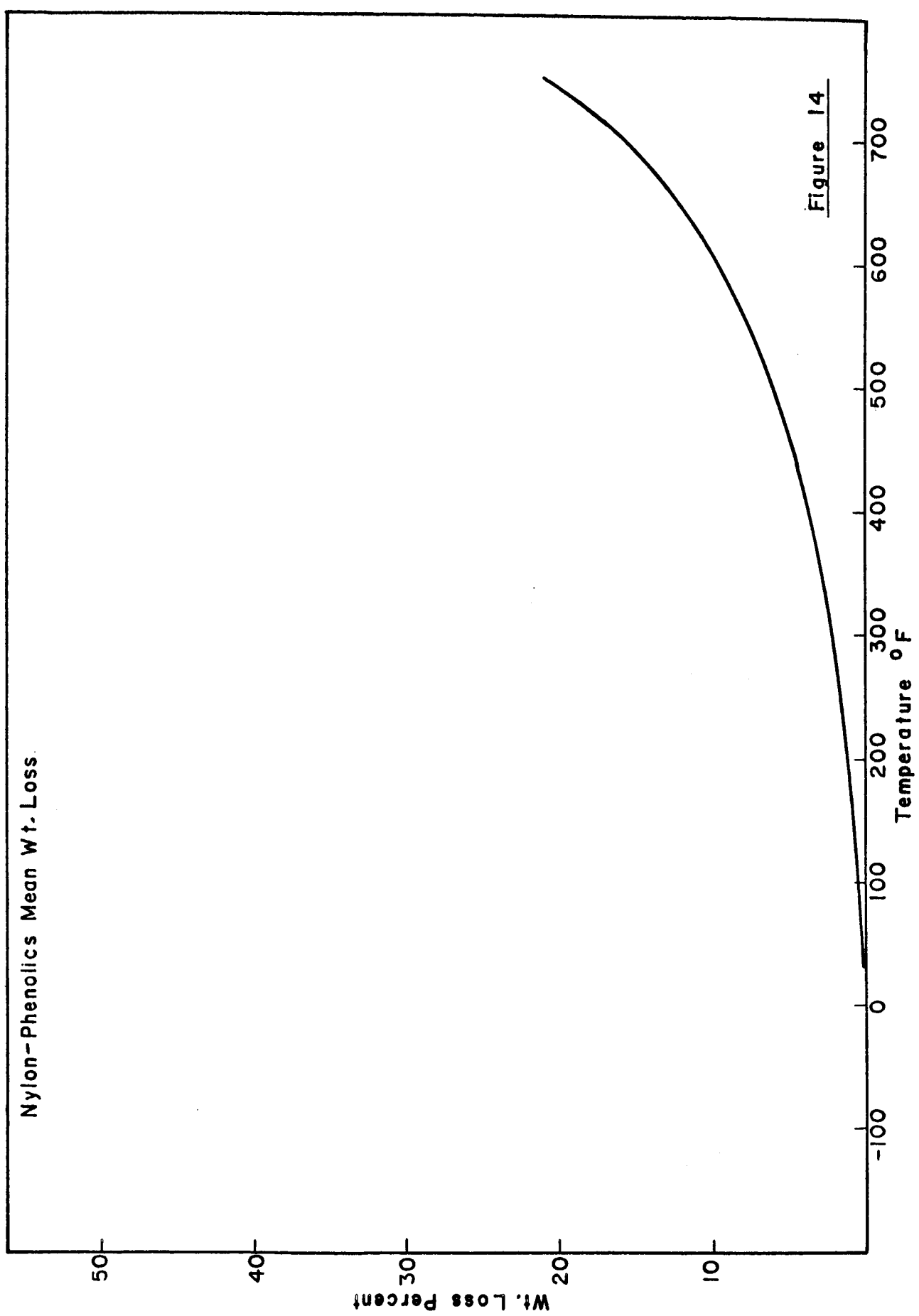


Figure 14

Silicone Resin A and Silicone Resin A Honeycomb Mean Weight Loss

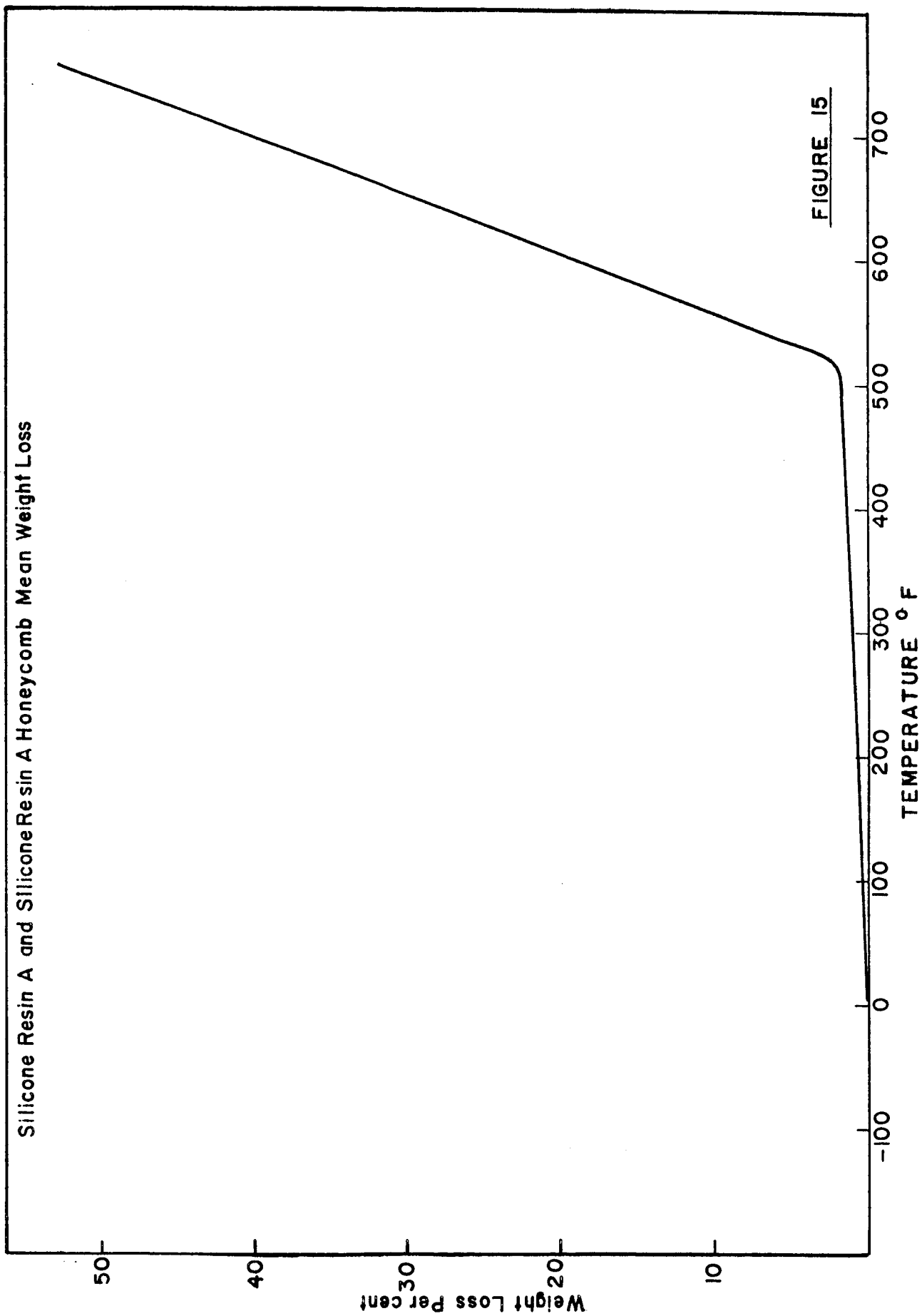


FIGURE 15

APPENDIX B

**PRELIMINARY
THERMAL EXPANSION
DATA**

THERMAL EXPANSION OF
HIGH DENSITY PHENOLIC NYLON

Temperature °F	In/In expansion $\times 10^{-3}$
-200	-7.15
-100	-5.10
0	-2.65
32	-1.75
104	1.00
212	7.39
284	12.23
320	14.55
356	17.19
374	18.00

TABLE 1

THERMAL EXPANSION OF
LOW DENSITY PHENOLIC NYLON

Temperature °F	In/In Expansion $\times 10^{-3}$
-200	-6.20
-103	-4.29
-4	-2.19
32	-1.29
104	.70
212	4.05
284	6.31
320	7.20
387	7.92

TABLE 2

THERMAL EXPANSION OF
FILLED SILICONE RESIN A

Temperature ° F	In/In Expansion $\times 10^{-3}$
-222	-20.58
-155	-16.57
32	- 3.50
133	3.56
154	4.99
251	10.59
324	14.89
387	18.10

TABLE 3

THERMAL EXPANSION OF
FILLED SILICONE RESIN MOLDED IN
HONEYCOMB IN THE "A" PLANE

Temperature °F	In/In Expansion $\times 10^{-3}$
-200	-16.71
-180	-15.48
-119	-11.61
-112	-10.92
32	- 2.70
162	4.59
221	7.85
239	8.61
378	15.10
435	17.06

TABLE 4

THERMAL EXPANSION OF
FILLED SILICONE RESIN MOLDED IN HONEYCOMB
IN THE "B" PLANE

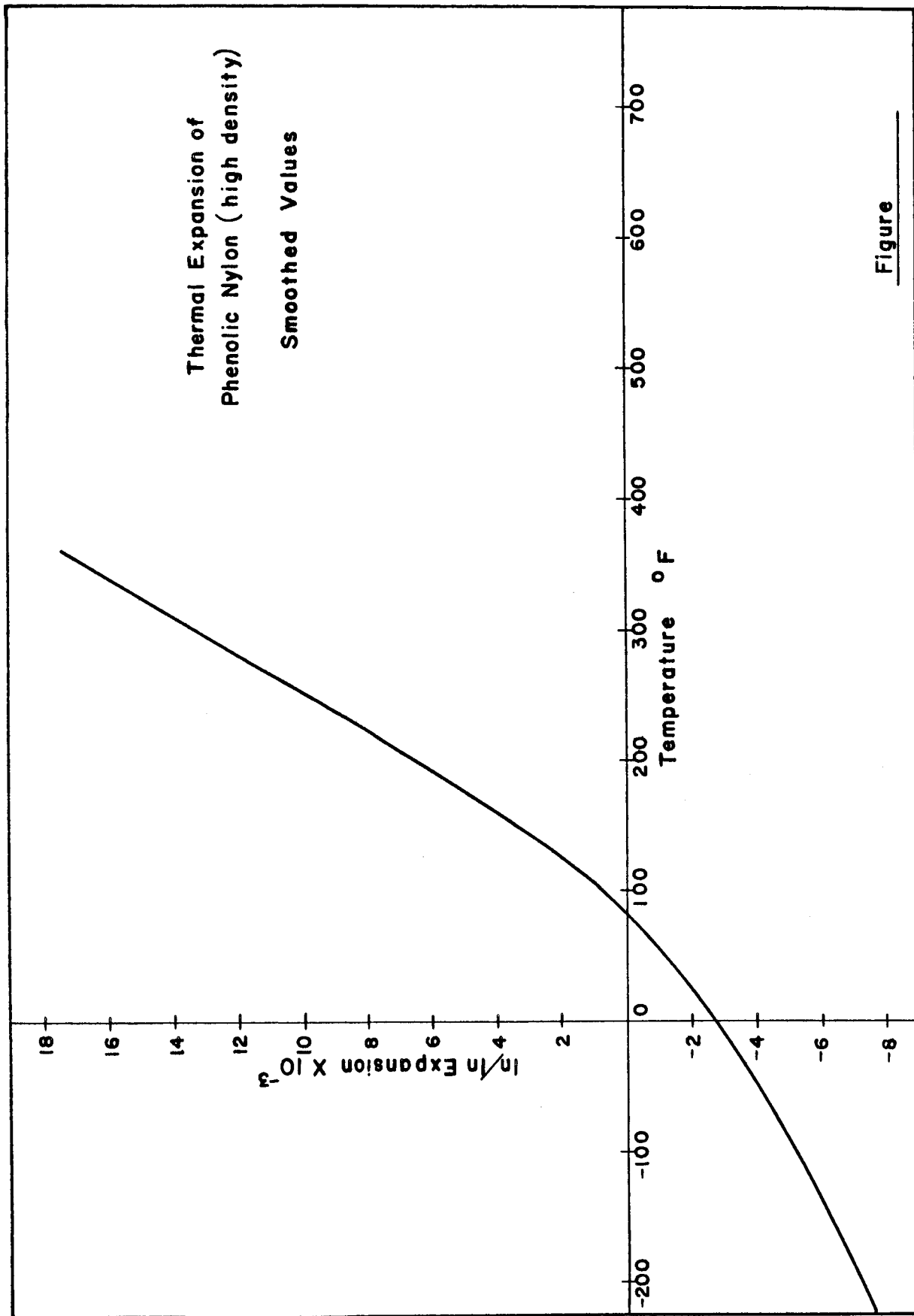
Temperature °F	In/In Expansion $\times 10^{-3}$
-200	-21.91
-180	-20.06
-119	-14.14
32	- 3.6
151	5.11
214	9.57
253	12.33
342	18.62
414	22.00

TABLE 5

THERMAL EXPANSION OF
FILLED SILICONE RESIN MOLDED IN HONEYCOMB
IN THE "C" PLANE

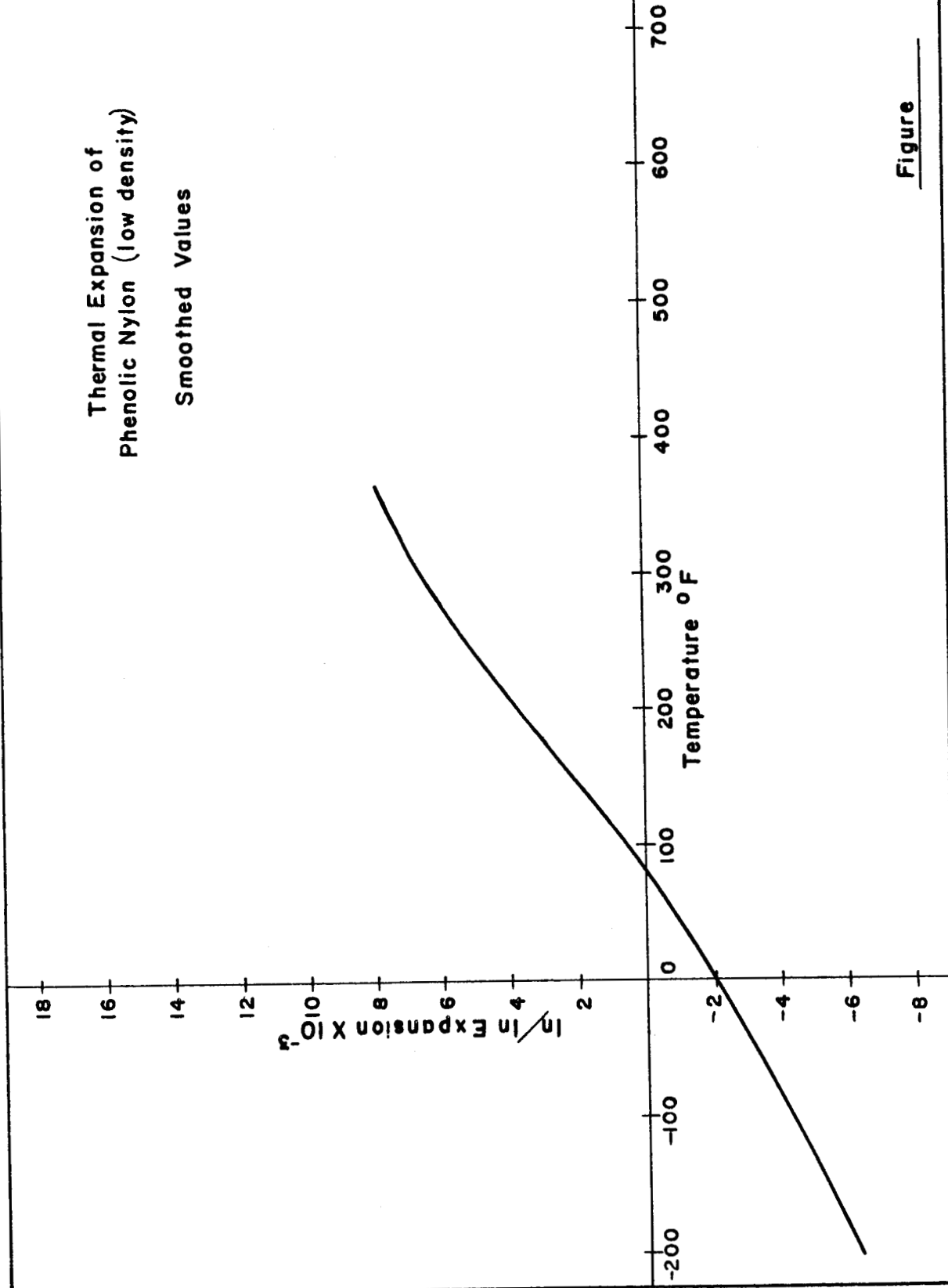
Temperature °F	In/In Expansion $\times 10^{-3}$
-200.2	-7.87
-148	-5.82
-109	-4.49
32	-1.04
144	1.28
149	1.42
156	1.61
160	1.70
248	1.69
252	3.12
342	6.99
354	5.54
369	5.92
381	4.75
381	4.75
390	5.93
392	4.93
396	7.65
397	4.96
405	7.71

TABLE 6

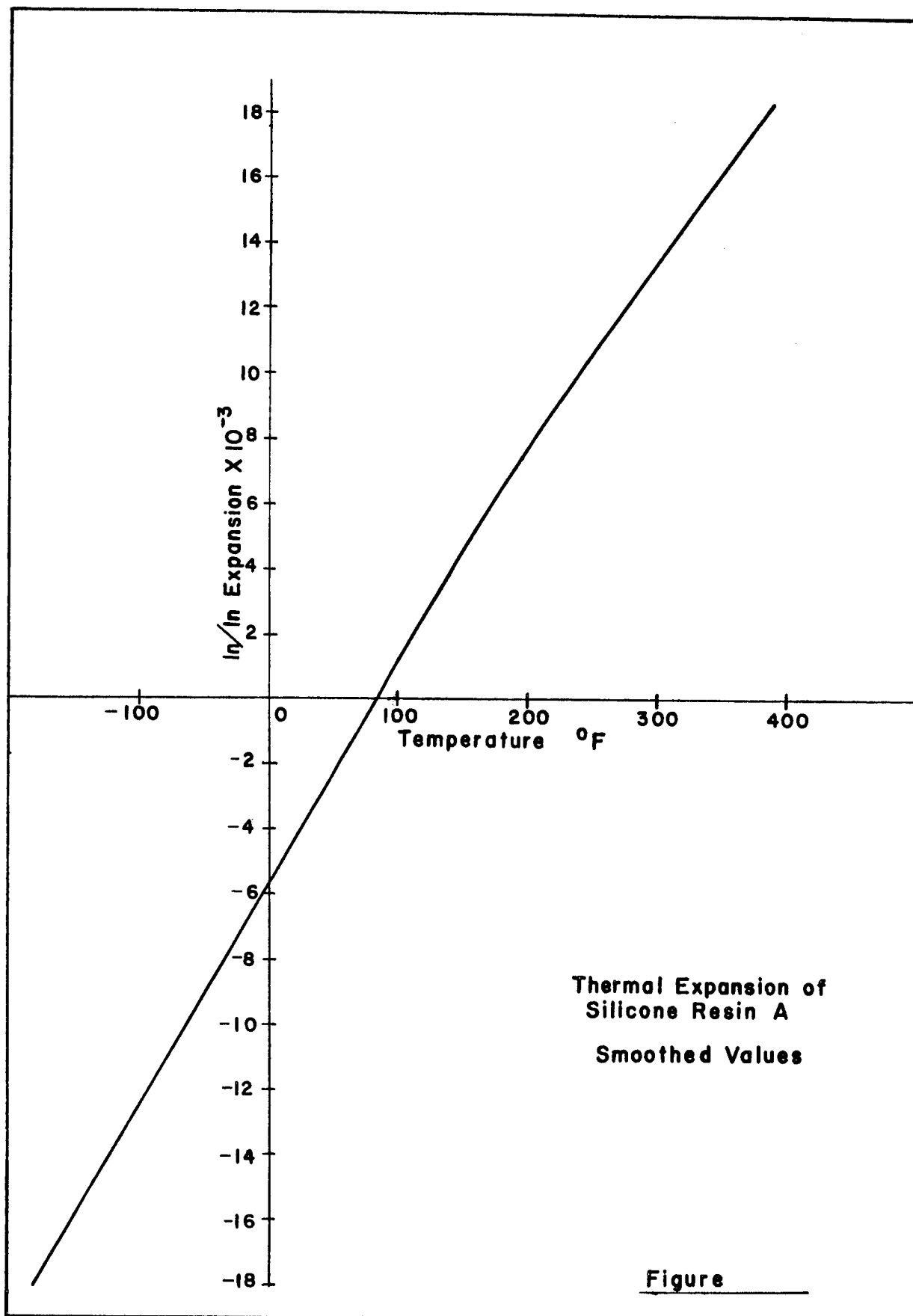


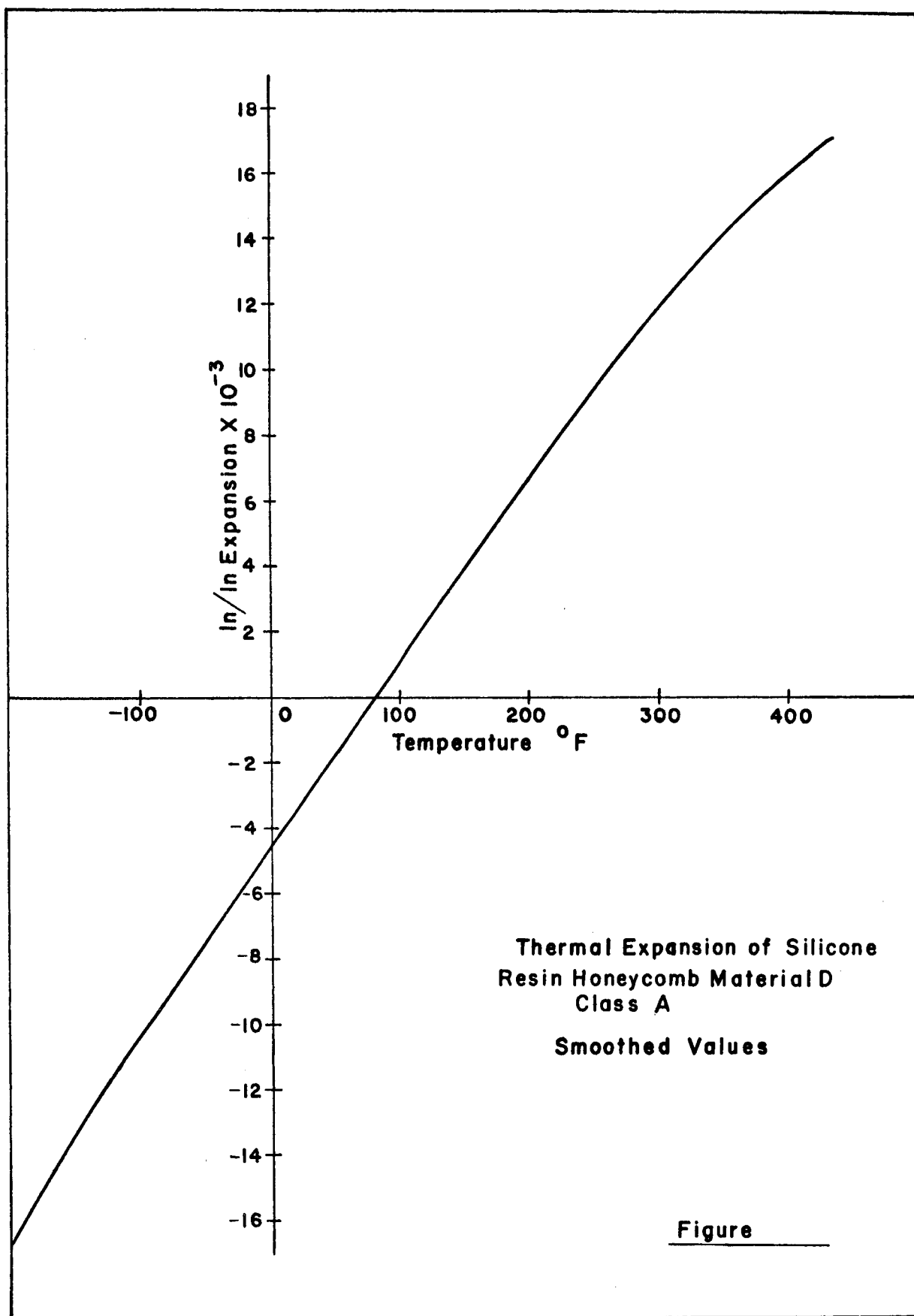
Figure

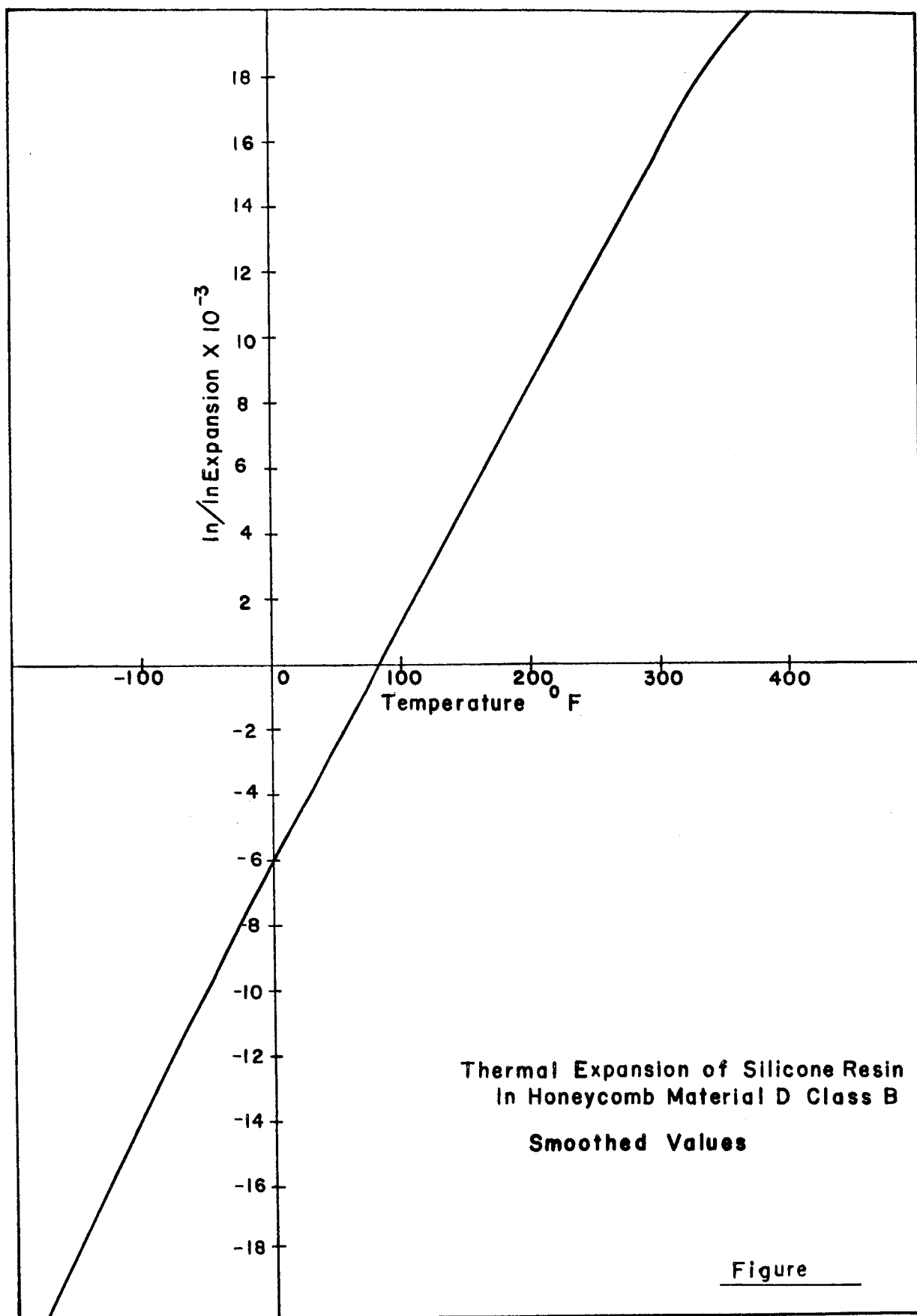
Thermal Expansion of
Phenolic Nylon (low density)
Smoothed Values

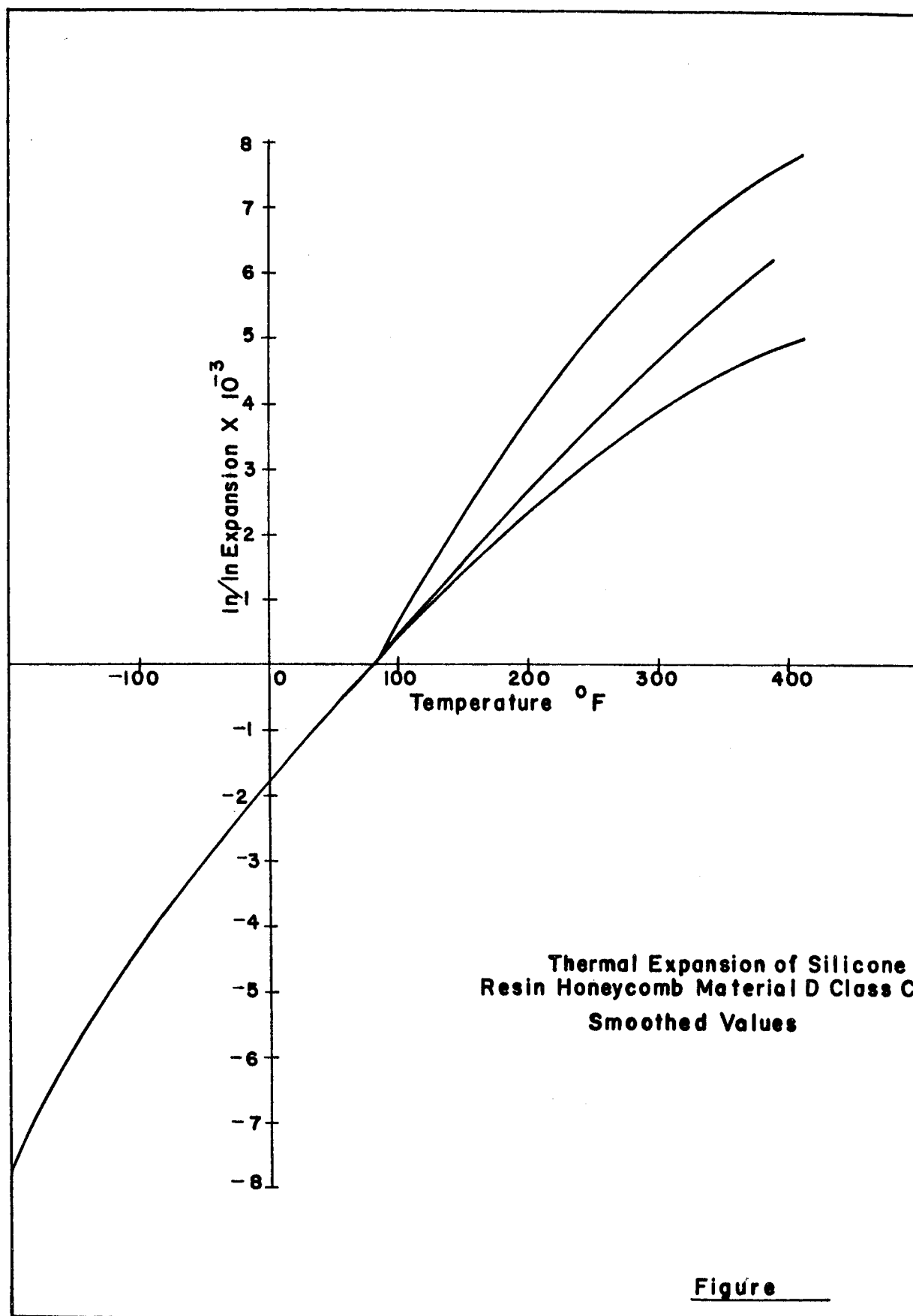


Figure









APPENDIX C

PRELIMINARY
THERMAL CONDUCTIVITY
DATA

THERMAL CONDUCTIVITY OF
HIGH DENSITY PHENOLIC NYLON

Temperature °F	"k" btu hr ⁻¹ Ft Ft ⁻² °F ⁻¹ x10 ⁻²
-184	14.76
-123	16.62
81	20.13
140	20.01
275	20.42
381	20.70
424	20.64

TABLE 1

THERMAL CONDUCTIVITY OF
LOW DENSITY PHENOLIC NYLON

Temperature °F	"k" btu hr ⁻¹ Ft Ft ⁻² °F ⁻¹ x10 ⁻²
-161	5.49
-90	6.14
88	7.45
334	7.61
403	7.51
415	7.33

TABLE 2

THERMAL CONDUCTIVITY OF
SILICONE RESIN A

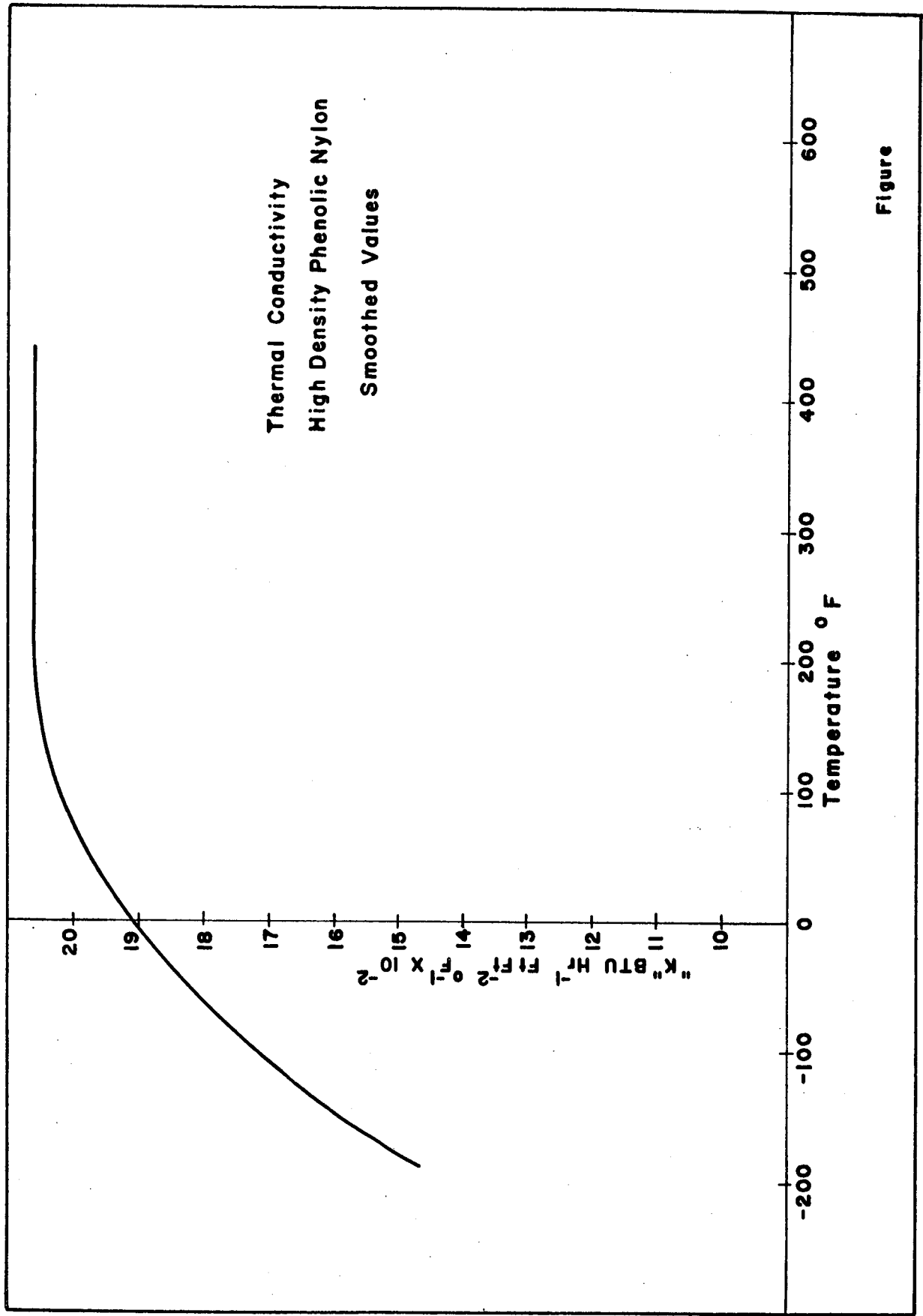
Temperature °F	"k" btu hr ⁻¹ Ft Ft ⁻² °F ⁻¹ x10 ⁻²
-197	5.00
-152	5.42
351	7.34
446	7.74

TABLE 3

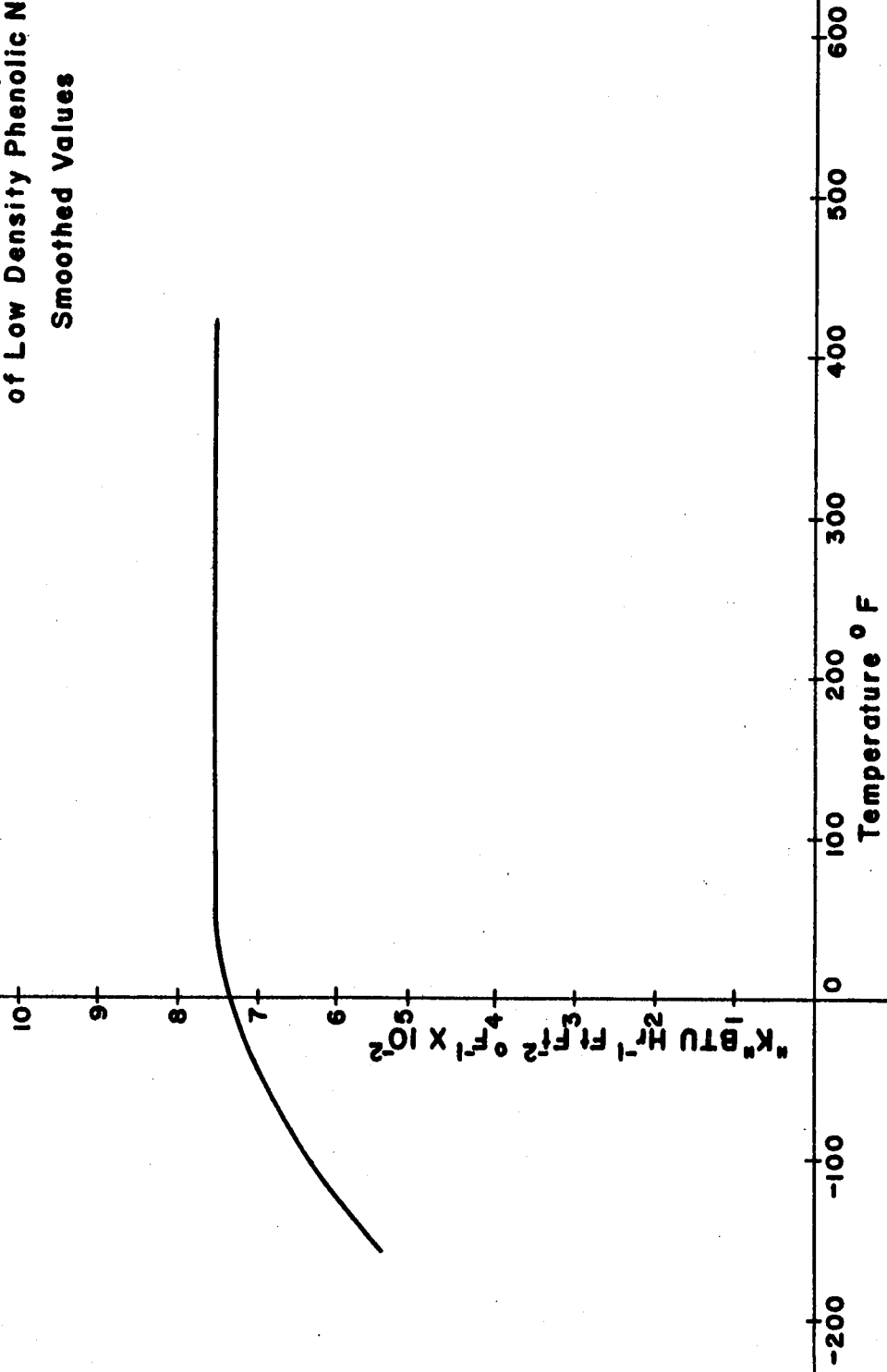
THERMAL CONDUCTIVITY OF
SILICONE RESIN MOLDED IN HONEYCOMB
IN THE "A" PLANE

Temperature °F	"k" btu in ⁻¹ Ft Ft ⁻² °F ⁻¹ x10 ⁻²
-188	5.38
-117	6.28
43	7.20
329	7.16
352	7.30

TABLE 4

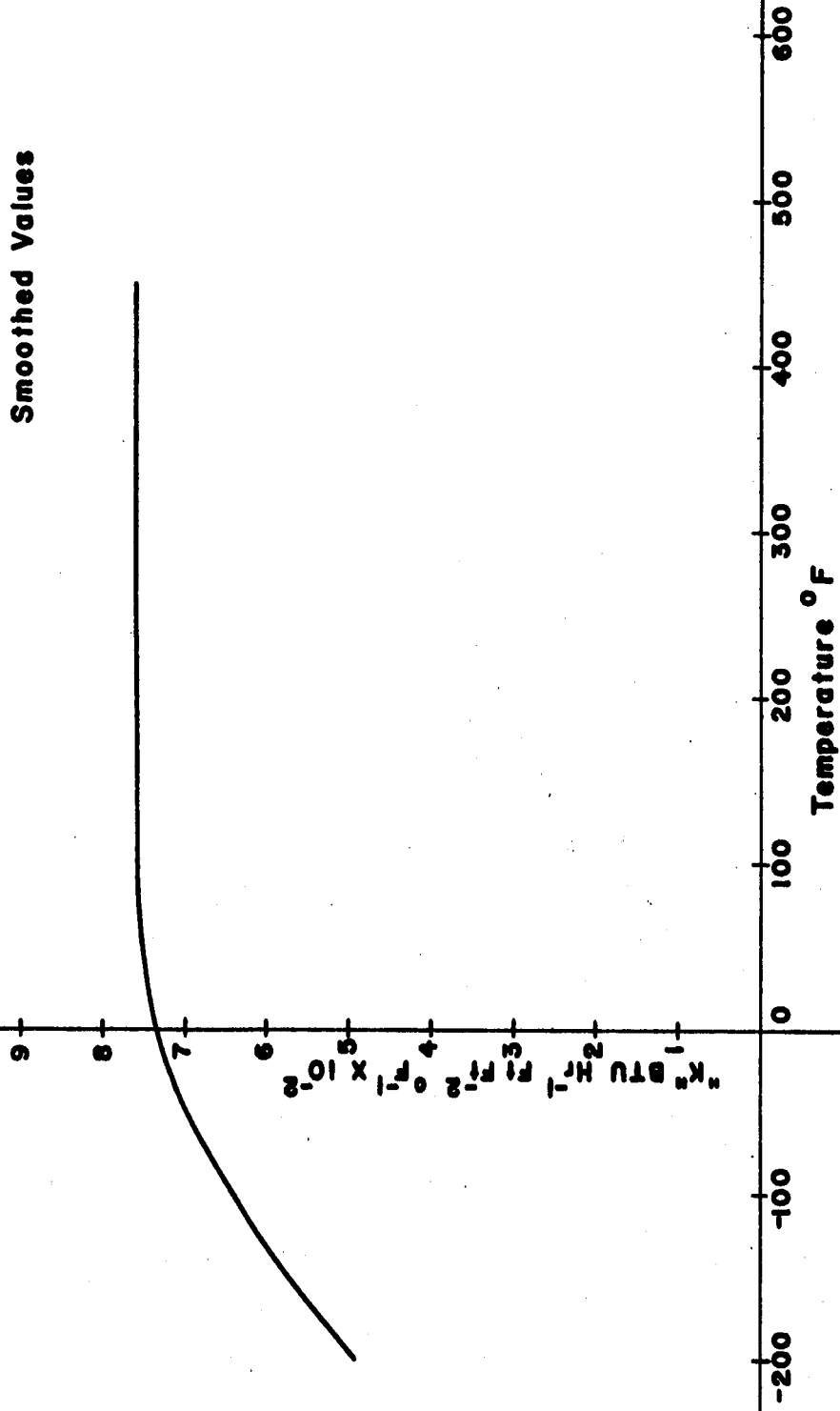


Thermal Conductivity
of Low Density Phenolic Nylon
Smoothed Values

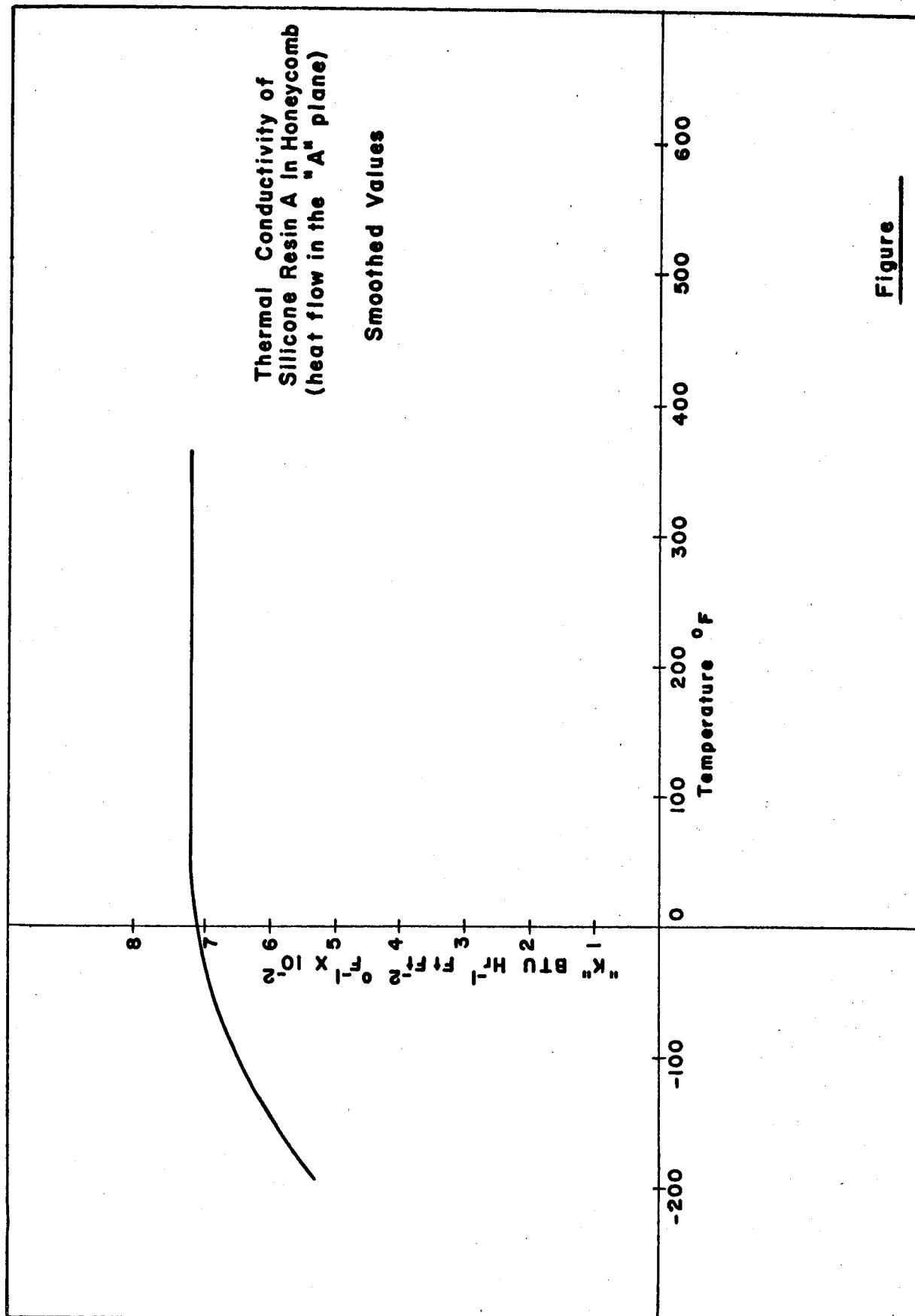


Figure

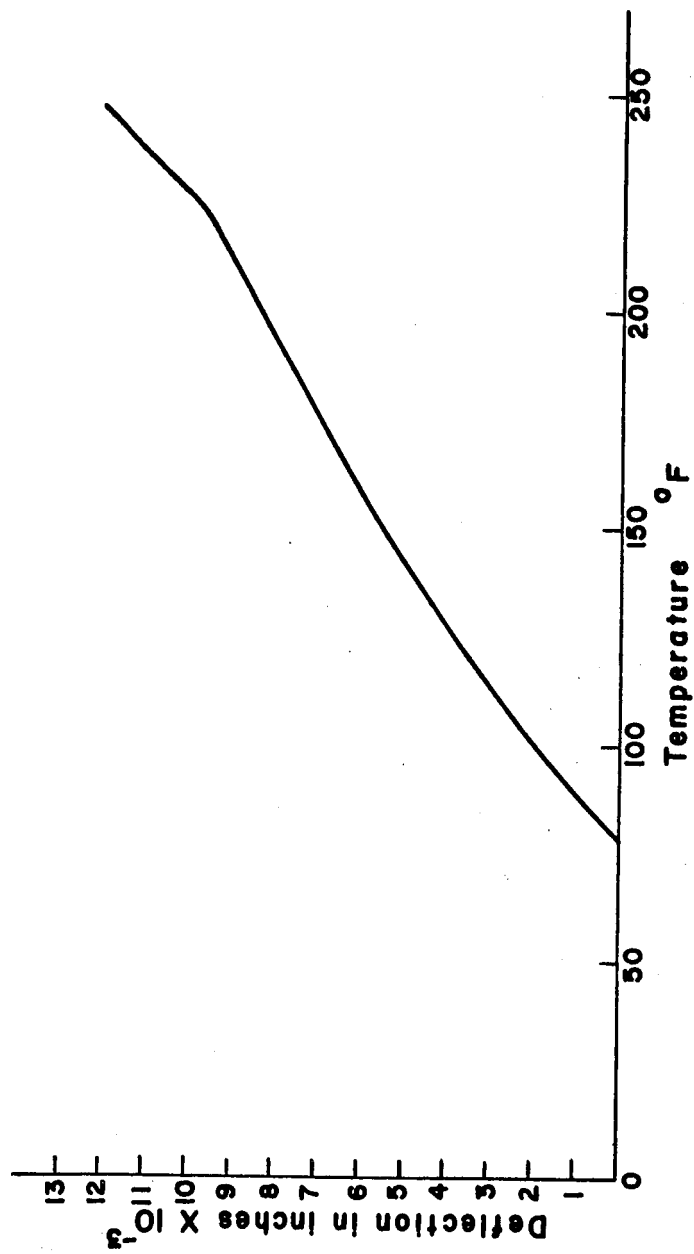
**Thermal Conductivity
of Silicone Resin A
Smoothed Values**



Figure



Heat Distortion Temperature
ASTM Test D-648
High Density Phenolic Nylon



Figure

APPENDIX D

PRELIMINARY
MECHANICAL PROPERTY
DATA

TABLE I

HIGH DENSITY PHENOLIC-NYLON MECHANICAL PROPERTIES

Tensile Strength

Temperature °F	Ultimate	Young's Modulus	Percent Total Elongation
-100°F	3075 psi	698,000 psi	0.4%
0°F	2190 psi	648,400 psi	0.4%
RT	2460 psi	436,000 psi	0.6%
200°F	2020 psi	149,000 psi	0.9%
300°F	1210 psi	73,500 psi	1.8%
350°F	500 psi	56,100 psi	1.6%
400°F	310 psi	22,800 psi	2.4%

Compressive Strength

Temperature °F	Ultimate	0.2% Offset Yield	Young's Modulus
-200°F	34,600 psi	19,200 psi	880,000 psi
-100°F	27,840 psi	18,640 psi	820,000 psi
0°F	28,440 psi	15,600 psi	710,000 psi
RT	20,400 psi	10,190 psi	532,500 psi
200°F	13,530 psi	4,260 psi	216,000 psi
300°F	5,520 psi	1,760 psi	80,000 psi
400°F	2,460 psi	1,060 psi	30,000 psi

TABLE II

LOW DENSITY PHENOLIC-NYLON MECHANICAL PROPERTIES

Tensile Strength

Temperature °F	Ultimate	Young's Modulus	Percent Total Elongation
-100°F	1180 psi	154,900 psi	0.8%
0°F	1250 psi	124,300 psi	1.1%
RT	1130 psi	113,700 psi	0.9%
200°F	1005 psi	72,200 psi	1.2%
300°F	915 psi	48,500 psi	2.3%
350°F	670 psi	42,000 psi	2.1%
400°F	334 psi	30,750 psi	1.0%

Compressive Strength

Temperature °F	Ultimate	0.2% Offset Yield	Young's Modulus
-200°F	5120 psi	--	213,000 psi
-100°F	3720 psi	2,890 psi	189,000 psi
0°F	3930 psi	2,660 psi	203,000 psi
RT	3740 psi	2,470 psi	145,000 psi
200°F	3020 psi	1,440 psi	111,500 psi
300°F	2940 psi	1,400 psi	51,000 psi
400°F	2400 psi	1,120 psi	31,600 psi